Accession No. M-3181

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. LII] SECTION A [No. 2

AUGUST 1960

Price Rs. 2 or 3 Sh. Annual Subscription Rs. 12

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY
SUPERINTENDENT, AND PUBLISHED
SCIENCES, BANGALORE.

ON THE SYSTEM AND ENGINEERING DESIGN OF THE GENERAL PURPOSE ELECTRONIC DIGITAL COMPUTER AT T.I.F.R.

By R. Narasimhan

(Tata Institute of Fundamental Research, Bombay)

Received March 14, 1960

(Communicated by Dr. S. S. Dharmatti, F.A.SC.)

1. Introduction

Since 1955, the Computer Section of the Tata Institute of Fundamental Research has been engaged in the development and construction of a large-scale electronic digital computer for doing scientific computations. As a preliminary to this, a pilot digital calculator was designed and completed in September 1956 and was kept in operation for about a year.[1] The design of the full-scale machine was started early in 1957 and its final assembly completed in February 1959. Unfortunately, owing to the lack of air-conditioning facilities, the work had to be suspended till almost the end of 1959. The actual testing was begun in mid-November 1959 with an auxiliary air-conditioning system and the computer was commissioned for routine work in the third week of February 1960. This paper describes briefly the main features of the system and engineering design of this digital computer. In a companion paper, some aspects of the circuitry will be dealt with.

The T.I.F.R. computer is a parallel, binary, asynchronous machine. It is controlled by a stored programme of single-address instructions and has a fast access ferrite-core memory consisting of 1,024 locations. The input to the computer is by means of a punched paper tape (5-hole commercial teletype tape) and the output can be either printed out directly or punched on a paper tape again.

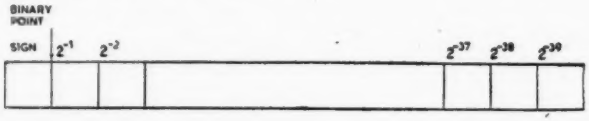
Both in the system and engineering design, the principal emphasis has been on reliability of operation and ease in maintenance. With this in view, the logical circuit types have been kept to the minimum consistent with flexibility and the wired circuits were put through a rigid acceptance test to check their performance under extreme operating conditions. For rapid fault localization and servicing, a large part of the computer has been assembled

in terms of functionally self-contained packaged units. Separate testing facilities have been set up for routine checking of these plug-in units.

The main computer assembly has 2,700 tubes (almost all of them double-triodes), 1,700 crystal diodes (germanium) and approximately 12,500 resistors. Since the computer is d.c. coupled throughout, few condensers are used and except in the case of two bias supplies, no circuit is transistorised. The total power consumption is about 18 K.W.

2. The Arithmetic and Control Logic

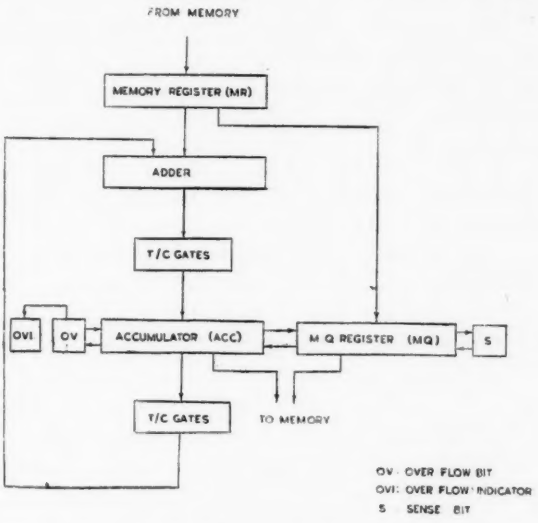
In the T.I.F.R. computer, all the internal operations take place in the binary notation and numbers are stored in the main memory as signed binary fractions restricted to the range (-1, 1). A number in its normal form consists of a sign (which is a 0 for positvie numbers and a 1 for negative numbers) followed by 39 binary digits (bits, for short) which give its absolute value as a binary fraction. The binary point is understood to be fixed immediately after the sign bit (*see* Text-Fig. 1). The complement form of a number is obtained by changing all its 1's to 0's and *vice-versa* ; the sign bit is left unaltered, however, in this process.



Text-Fig. 1. Number Representation (Binary Fraction).

A schematic diagram of the arithmetic unit is shown in Text-Fig. 2. It consists of an adder, a memory register and two (double rank) shift registers (the accumulator and MQ-register, respectively) and a pair of true/complement gates. The adder is of the fast logical type and incorporates in itself special carry by-pass facilities to speed up the carry propagation time.[2] These cut down the addition time to about one-third of what it would otherwise have been. The contents of the accumulator are presented to the adder either in the true or the complement form depending on whether the operation called for is addition (multiplication) or subtraction (division) respectively. In some cases the result of a subtraction needs to be recomplemented to obtain the number in its true form. To simplify this procedure, facilities have been built into the adder so that its output can be gated into the accumulator either in its true or complement form. Also the particular design of the adder used makes it especially simple to obtain the logical product of the adder inputs and this is taken advantage of in the Collate order.

The absolute value representation of numbers makes the multiplication and division logic very simple and straightforward. In both cases, the operation is carried out treating the numbers as positive quantities. The proper signs are written into the accumulator and MQ-register in the end. The incorporation of an extra bit, called the *Sense bit* (2^{-40} stage of MQ) is believed



Text-Fig. 2. Schematic of Arithmetic Unit.

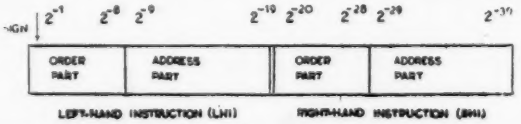
to be a unique feature of this computer. In multiplication, the discrimination for add-shift/shift is obtained from this sense bit rather than from Q^{-39} as is normally done. Similarly, in division the quotient bits are written into the sense bit rather than into Q^{-39}. Thus both multiplication and division involve 40 shifts (instead of the usual 39). This has the major advantage that normal division is unrounded (*i.e.*, is correct up to and *including* the 2^{-39} stage). It is expected that this feature will have special advantages in multiple precision work. In shift operations, the sense bit functions like an extension to the MQ-register on its right end.

All *proper* arithmetic operations should result in numbers which again fall within the range $(-1, 1)$. But there are no built-in checks to detect improper ari hmetic operations. It is, in the main, the responsibility of the programmer to see that numbers are confined to the admissible range, by proper scaling, all the time. However, to help him in doing this, an extra bit, called the overflow bit, has been provided at the left end of the accumulator. In the case of a genuine overflow (*i.e.*, addition of numbers with the

same signs, or subtraction of numbers with opposite signs) it is fed into the overflow bit and an overflow indicator, OVI (which normally stays 0), is set to 1. This is not reset to 0 unless explicitly called for by the programmer. A "jump on overflow" order enables the programmer to make use of this information in variable scaling of numbers or in normalising in floating point arithmetic. Also, in ordinary shift operations, the overflow bit functions as an extension to the accumulator on the left and the OVI becomes operative when a 1 is shifted into the overflow bit.

A "round-off" order enables the accumulator content to be rounded off by adding a 1 or 0 to its least significant bit according as the MQ content is greater than or less than $\frac{1}{2}$.

As has already been mentioned, the T.I.F.R. computer is of the asynchronous, single address type. The details of its control logic are effectively determined by these two features. A coded instruction in the machine requires 20 bits for its specification: (the first 9 bits for its *order* part and last 11 bits for its *address* part). Because the word length in the memory is 40 bits, instructions are stored in pairs in each memory location. They are identified as the left-hand (L.H.I.) and right-hand (R.H.I.) instructions in that location (*see* Text-Fig. 3). A complete control cycle consists of 3 parts: (1) an *instruction cycle*, where a (next) pair of instructions is brought from the memory to the instruction register ; (2) an *execution cycle A*, where the left-hand instruction is executed and (3) an *execution cycle B* where the right-hand instruction is executed. The sequencing within the cycles is effected by means of 4-state sequencing units similar to the ones used in ORDVAC type machines.[3] The static control levels are obtained by partial decoding of the order bits of an instruction. As far as possible, the micro-operations are done in parallel so as to minimise the number of sequencing steps required.



TEXT-FIG. 3. Allocation of bits in a pair of instructions.

One built-in B-register (of 11 bit length) is available for address modifications. The shift counter is also similar to the one used in ORDVAC but an improved gating logic has enabled its speed to be increased appreciably.[4]

In addition to the unconditional jump order, 6 types of conditional jump orders are available, *viz.*, jump if accumulator sign bit is 0/1 ; jump if MQ-sign bit is 0/1 ; jump if the overflow indicator is 0/1. In the case of the last order, the control resets the overflow indicator to 0.

Table I gives a summary of the order types and variants built into the computer.

TABLE I

Order types and their variants

	Type	Variants	
1. Arithmetic orders	Add	Hold Acc. Signed/Abs. Val.	Clear Acc. Signed/Abs. Val.
	Subtract	"	"
	Multiply Unround	"	"
	Multiply Round	"	"
	Divide	"	"
	Collate	"	"
	Round off	"	"
2. Shift orders ..	Shift Rt. Acc.	Hold Acc.	Clear Acc.
	Shift Lt. Acc.	"	"
	Shift Rt. Acc.-MQ	"	"
	Shift Lt. Acc.-MQ	"	"
	Shift Lt. Acc.-MQ (also Q°)	"	"
3. Store orders ..	Store Acc.	Hold Acc-MQ	Clear Acc.
	Store LHA Acc.	"	"
	Store RHA Acc.	"	"
	Store LHA-RHA Acc.	"	"
	Store MQ	"	"
	Transfer to MQ	"	"
	Transfer to B-Reg.	"	"
4. Jump orders ..	If A° = 0	To LHI	To RHI
	If A° = 1	"	"
	If Q° = 0	"	"
	If Q° = 1	"	"
	If OVI = 0	"	"
	If OVI = 1	"	"
	Unconditional	"	"
5. Miscellaneous orders	Conditional Stop	Stop	
	Input	..	
	Output	Tape/Drum	
		Punch/CRT/Drum	
Operating Speed ..	Instruction cycle:	20 μ-sec.	
	Execution cycle— Add/subtract:	45 μ-sec.	
	Mult./Divide:	500 μ-sec.	
	Shift n:	$14 + 11\,n$ μ-sec.	

3. THE MEMORY

The internal memory of the T.I.F.R. computer consists of a 3-dimensional ferrite-core matrix (made up of 40 planes), 40 output amplifiers, diode decoding nets for address selection and drive circuits for reading and writing. The matrix assembly was purchased from Mullard and Co., England. The read-rewrite logic is essentially the same as that described by Papian originally for the MIT computer.[6] Both amplitude and time discrimination (Strobing) is used at the output end to increase the signal/noise ratio. The read output is gated into a set of memory flip-flops which also function as the memory register of the arithmetic unit. The input to the memory can be either from the accumulator or the MQ-register. While storing from the accumulator, either the entire content of the register or only the address part (either the left-hand or right-hand address alone or both) can be written in. Except for the initiating trigger, the memory sequencing is completely independent of the rest of the computer control. The duration of a single memory read-write cycle is approximately 15 μ-seconds.

Provision has been made for incorporating a second core-matrix of equal capacity at a later stage thus doubling the internal store.

4. THE POWER SUPPLY

The power requirements of a large-scale parallel electronic digital computer pose some severe problems normally not encountered in conventional electronic systems of a similar size. The power supply system, while large in capacity (usually of the order of 20 K.W.), has to be at the same time (1) very highly reliable and rugged ; (2) well stabilised for not only the usual line voltage fluctuations but for load switchings at very high repetition rates (calling for a response time of the order of a few μ-seconds on the part of the regulator for almost 0 to full-load switching) and (3) fully protected against partial failures by effectively fool-proof protective interlocks. The power supply for the T.I.F.R. computer has been designed and constructed to satisfy all the above requirements and has been under satisfactory operation for several months.

The input to the power supply is from 3-phase, 4 wire, 50 cycles, 230 volt mains with a nominal rating of 40 KVA. Two regulators are provided, one an electromechanical unit capable of handling up to 20 KVA and is intended principally for the tube heater supplies. The other is an electronic stabilizer for the high tension busbars in the computer.

The filament transformers are signle-phase units, each capable of supplying 200 amps. at 6·3 volts. 10 such transformers are used in all to supply the

heater power for the various units of the computer. A relay controlled system allows gradual application of filament voltages to the tubes and provides the necessary delay before the application of plate voltages.

The d.c. high tension levels used in the computer together with their full-load currents are as follows:

-300 V : 18 amps.

-150 V : 4·5 amps.

$+110$ V : 10 amps.

$+150$ V : 5 amps.

$+200$ V : 7 amps.

$+300$ V : 2 amps.

These voltages are stabilised to within 1% for line voltage fluctuations and to within 2% for 0 to 100% load switching with a recovery time of the order of a few μ-seconds. The electronic regulator consists of grid controlled thyratrons used in a 3-phase half-wave circuit and a "stiff" filter with a large output capacitance (of the order of a few hundredths of a farad for each level) to provide the necessary recovery time. A specially developed pulse-shifting circuit fires the thyratrons.

5. Engineering Design

Figures 4 and 5 show an overall view of the computer assembly and power supply units. The main computer assembly is housed in a steel rack $18' \times 2\frac{1}{2}' 6'' \times 8'$ which has been fabricated out of modules of size $4' \times 2\frac{1}{2}' \times 8'$. Each module has a pair of steel doors (of size $2' \times 6'$) on either face to provide accessibility to the circuits. For ease in maintenance, single layer mounting has been adopted for the wired panels except in a few instances where a second layer has been wired on swing-out panels. The information flow is along the horizontal with the arithmetic unit in the centre flanked on either side by the control and the memory units. The bits in each functional unit occupy the modules from top to bottom. The lower 18" of the entire assembly house the filament transformers and some of the output capacitors while also serving as an air plenum for the forced-air-cooling system. Cool air (at approximately 20° C. and a total flow of 6,000 c.ft./min.) is fed into the computer at the two ends, channelled through the various modules and exhausted into the room from the top. Exhaust fans mounted along the length of the computer

on top help to maintain uniform distribution of the cold air inside the computer assembly.

The power unit is housed in two independent racks, one containing the contactors, a.c. regulators, variacs, transformers and output capacitors, and the other containing the thyratrons, pulse control units, control and voltage monitoring relays. The electronic circuitry is mounted on pull-out chassis to facilitate servicing.

6. AUXILIARY EQUIPMENT

As has already been mentioned, the information input into the computer is by means of punched paper tapes and the output from the machine can again be either punched on tapes or directly printed out. Currently, commercial Olivetti Type T2Pr/T2CN reperforators and page printers are being used for this purpose. A Ferranti Mark II tape reader has been tried out but a much faster servo-controlled Potter Model 903 tape reader is in an advanced stage of testing and is expected to be available for use very soon. A high speed Creed Model 75 page printer/reperforator has also been acquired with a specially built-in code to facilitate direct binary to decimal conversion. This, together with the Potter tape reader, it is expected, will provide very adequate input-output facilities for the computer.

A manual control console has been set up to serve as a very flexible input/output/control unit to regulate and monitor the operation of the computer. Facilities are available for single shot operation; for slow external triggering at approximately one cycle per second and for manual sexadecimal input into the MQ-register with the help of a diode decoding net operated from a keyboard. Neon indicators enable visual monitoring of the contents of all the registers.

For routine maintenance checking and also for servicing of the various plug-in units used in the computer, a comprehensive test rack has been built. Detailed and systematic d.c. checking of the units can be carried out with great ease with the help of the test rack and complete test schedules have been worked out for each unit to systematise the test procedures.

A cathode ray tube (C.R.T.) display system has been developed to serve as an auxiliary output to the computer for fast analogue and digital display of both graphs and alpha-numeric symbols. A pilot version has already been built and successfully operated.[7] The more elaborate final unit is under assembly and is expected to be available for routine use in a few months' time.

Work on the development of a magnetic drum to serve as a large capacity back-up storage has been going on concurrently with the assembly of the main computer. The final specifications of the drum have been drawn up and the mechanical assembly is under fabrication. Logical design of the drum control and read-write circuits are being finalised. When this facility is made available, the total computer storage capacity will increase eight-fold.

7. Operational Experience

Since the completion of the computer assembly early in 1959, the various parts of the machine have been under operation for almost a year now. The operational and maintenance experience gained over this period indicate that with adequate *routine* maintenance, the computer should give reliable, trouble-free operation over long periods of time continuously. It has not been possible so far to collect systematic statistics of failure rates, of types of faults and of time lost in unscheduled servicing. However, it may be mentioned that in general the component failures have been remarkably few in number. Less than 5% of the tubes have had to be changed (and this mostly for loss in emission) and there have been resistance failures only in the case of 2 or 3 types of resistors.

Comprehensive test programmes have been designed to check each of the functional units under a variety of input-internal state configurations. These have proved to be of invaluable aid in fault location and in routine checking. By means of test programmes every single core in the memory matrix has been tested for reading and writing under the most adverse operating conditions.

It is proposed to operate the computer, at the first instance, on an 8-hour shift daily. The first 3 hours will be devoted to scheduled maintenance and the remaining 5 for useful computing. A programming manual has been prepared to assist machine users in programming their own problems.

8. Summary

This paper gives a brief description of the system and engineering design of the general purpose electronic digital computer that has been developed and built in T.I.F.R., Bombay. This computer is a parallel, binary, asynchronous machine with a ferrite-core matrix fast memory of 1,024 words. The arithmetic is in the fixed point binary system with a number length of 40 bits. The computer incorporates one B-register for address modification and several other special features such as overflow indication, carry bypass, etc., Input-output is by means of punched paper tape. An auxiliary output in the form of a CRT display has been developed and a magnetic drum to serve as a back-up store is being designed.

9. ACKNOWLEDGMENTS

A large-scale general purpose digital computer is perhaps the most complex electronic equipment designed so far to function as one integrated centrally controlled unit. Needless to say, the development, design and construction of such a system calls for a very high degree of organisation and planning and for the co-ordinated efforts of a large group of individuals. For the successful completion of the T.I.F.R. computer the following have been responsible: The overall logic and engineering system design as well as the planning and co-ordinating of the project was the principal responsibility of the author. The detailed design of the control and arithmetic logic and its physical realization in terms of circuitry as well as the design and construction of the auxiliary control and test equipments were entirely carried out by B. K. Basu, assisted by K. Bakhru, M. M. Dosabhai, Miss V. K. Joglekar, B. B. Kalia, R. R. Nargundkar, S. V. Rangaswamy, P. V. S. Rao and V. M. Vengurlekar. For the memory assembly and associated circuits, S. P. Srivastava was responsible, assisted by C. V. Srinivasan and T. R. N. Rao. The entire development, design and construction of the power supply system was carried out by M. M. Farooqui, assisted by D. F. Cooper, R. Y. N. Iyengar and R. K. Shah.

Special acknowledgment is made here of the help rendered by the Development and Production Unit of the Atomic Energy Establishment, Trombay, in wiring the plug-in units and in the fabrication of some of the pulse transformers. Also, the co-operation of the Institute workshop personnel at the various stages of the computer fabrication is gratefully acknowledged. Special mention should be made of the untiring and enthusiastic co-operation of Junior Mechanic, R. P. Thosar, over the past 5 years.

Grateful acknowledgment is also made of the keen interest shown by Dr. D. Y. Phadke in the project.

10. REFERENCES

1. "The Pilot Digital Calculator at T.I.F.R., Bombay," *The Digital Computer Newsletter*, January 1957.

2. Rao, P. V. S. and Basu, B. K. "A fast logical adder," *Tech. Report* (unpublished).

3. *ORDVAC Manual*—University of Illinois, 1952.

4. Basu, B. K. and Rao, P .V. S. "A modified gating logic to improve the speed of operation of double rank counters," *Proc. Ind. Acad. Sci.*, 1957, **46**, 354–59.

5. ——— and Bakhru, K. "The input-output system of the T.I.F.R. computer," *Ibid.*, 1957, **45**, 231–39.

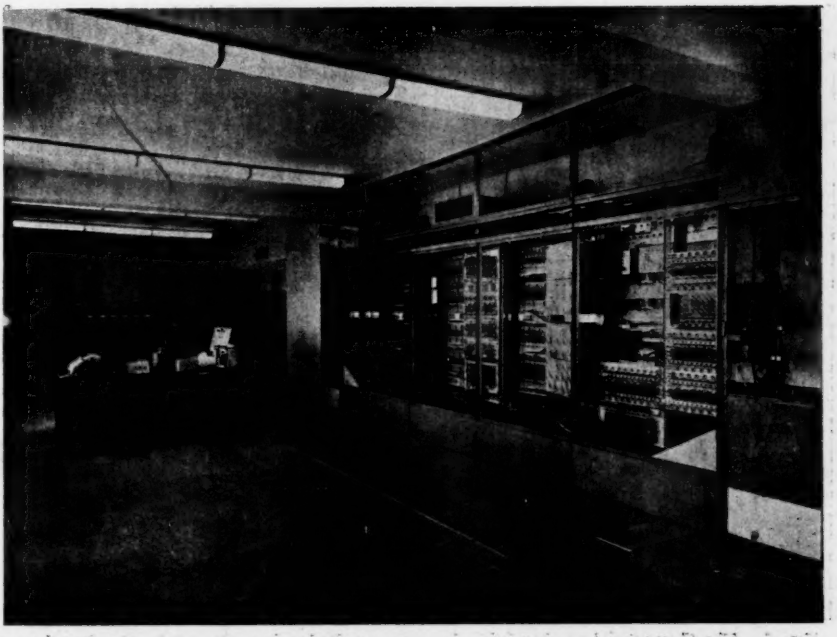


FIG. 4. The Computer Assembly (with doors removed) showing the Manual Console and the power supply units.

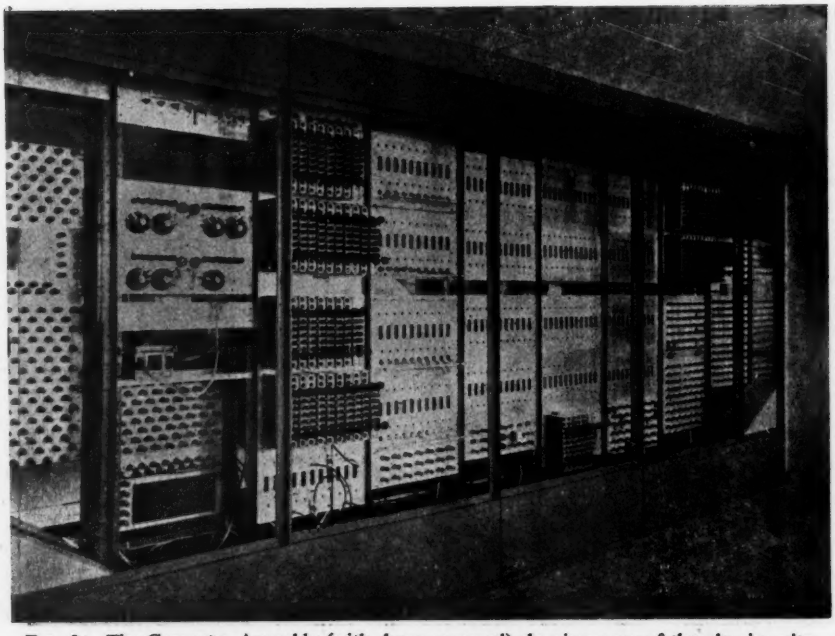


FIG. 5. The Computer Assembly (with doors removed) showing some of the plug-in units.

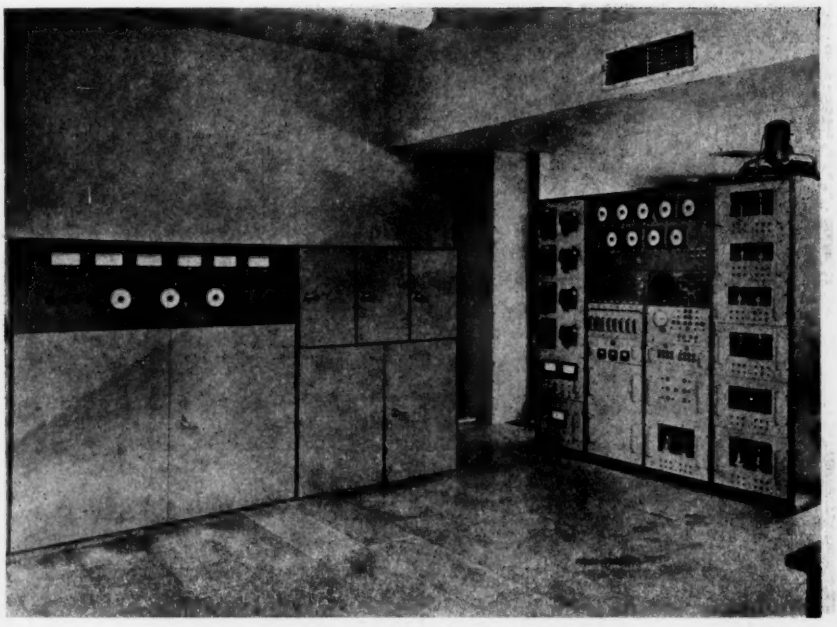


FIG. 6. The power supply units of the Computer.

6. Papian, W. N. .. "The M.I.T. magnetic core memory," *Proc. Eastern Joint Comp. Conf.*, December 1953 (1954), p. 37.

7. Rao, P. V. S. .. "A character display system for use as a digital computer output," *Note, Rev. Sci. Inst.*, 1959, **30**, 749–50.

STUDIES ON METALLIC HALIDE DIOXANATES—III

Dioxanates of Cobalt (ii) and Nickel (ii) Chlorides

MISS SOSAMMA CHANDY AND S. S. MOOSATH

(Applied Chemistry Department, University of Kerala, Trivandrum)

Received May 19, 1960

(Communicated by Dr. M. R. A. Rao, F.A.SC.)

INTRODUCTION

DIOXANE complexes of many metallic halides have been investigated by several workers. Rheindboldt *et. al.*,[1] in the course of their extensive studies on the dioxanates of the halides of mono, di and trivalent metals, have reported cobalt iodide to form the tri and monodioxanates and nickel chloride to form the monodioxanate. Some of these observations have been independently recorded by Juhaz and Yntema.[2] The information available about these complexes is very scanty. The present paper describes the method of isolation, characterisation and stability of cobalt and nickel chloride monodioxanates. A stable, lower dioxanate of each of these chlorides has also been isolated.

Different procedures have been adopted for the preparation of the dioxanates. Most of the workers have recognised the effect of moisture and have taken special care to exclude moisture during the various steps of preparation and stability studies. The methods followed by Crenshaw *et. al.*,[3] Juhaz and Yntema,[2] Kelley and McCusker[4] and McCusker *et al.*[5] do not ensure complete purity of the products.

An improved method[6–8] of preparation has been reported where a solution of the halide in benzene, carbon tetrachloride, carbon disulphide or alcohol is mixed with dioxane and the dioxanate, which is usually insoluble in the solvent, is isolated. Moosath and Rao[9] have successfully isolated hexachloroceric acid in a crystalline form from a solution in dioxane. Their technique has been adopted by Nair and Moosath[10–12] for the preparation of several metallic chloride dioxanates. The metallic oxide is suspended in dioxane and treated with hydrogen chloride gas. The solution is filtered and the filtrate cooled to crystallisation. The device of Moosath and Rao of washing the product with petroleum ether, to remove excess free dioxane, has also been adopted with advantage.

The method of Nair and Moosath for the preparation of metallic chloride dioxanates had to be slightly modified in the present studies. This was necessary because these dioxanates are only sparingly soluble in dioxane saturated with hydrogen chloride and are not easily crystallised out from the solution by cooling. However, this difficulty has been overcome by concentrating the dioxane solution by repeatedly washing with petroleum ether and then crystallising.

Cobalt (ii) and nickel (ii) chloride dioxanates have similar properties and are very stable. When evacuated at 1 mm. pressure at 110° C. the cobalt compound suffers a loss in weight of 5 per cent. in three hours and the nickel compound, 7 per cent. during the same period. Lower dioxanates, $CoCl_2 \frac{1}{2} C_4H_8O_2$ and $NiCl_2 \frac{1}{2} C_4H_8O_2$, with the halide to ether ratio 2:1, are precipitated by ether from the alcoholic solution of the monodioxanates. It may be pointed out that the same analytical values will be obtained if the halides are precipitated with one mole of solvation, as the molecular weights of $MCl_2 \frac{1}{2} C_4H_8O_2$ and $MCl_2 C_2H_5OH$ are very close to each other. Since the complexes are fairly stable when evacuated at 110° C. and 1 mm. pressure, it can be assumed that alcohol of solvation is absent. A similar compound for cadmium, $CdCl_2 \frac{1}{2} C_4H_8O_2$ has been reported[2] by earlier workers.

Experimental

Pure cobaltous chloride (50 g.) was dissolved in about 600 ml. water and the hydroxide precipitated with dilute sodium hydroxide solution. The pink precipitate was rapidly filtered and washed free of alkali. It was then washed several times with alcohol and dried to constant weight in a vacuum oven at 90° C. The powdered dry material, which was obtained as a black powder, was stored in a stoppered vessel in a desiccator containing sodium hydroxide pellets. Pure nickel nitrate (50 g.) was dissolved in about 800 ml. water and the hydroxide precipitated with dilute sodium hydroxide solution. The apple-green nickel hydroxide was filtered off and treated as above. Dioxane, ethanol and petroleum ether (40–60°) were purified and dried by standard methods.

Cobalt (ii) chloride dioxanate.—Cobaltous hydroxide (5 g.) was suspended in 100 ml. dioxane and treated with dry hydrogen chloride gas. Within 15 minutes, formation of the complex was indicated by the appearance of a bluish colour to the liquid. The reaction flask was kept cooled in water to prevent excessive rise in temperature. After bubbling the gas for 90 minutes, the flask was disconnected, stoppered and left overnight. The solution was filtered through a sintered funnel under dry conditions. The

clear, sky-blue filtrate was left in the refrigerator for crystallisation. The residue on the funnel after washing several times with petroleum ether was found to be pale pinkish-grey in colour. But on passing dry air, the colour changed to pale lavender. This colour was lost on keeping for two hours, the substance acquiring the original pinkish-grey colour which was found to be permanent. [Found : (Per cent.) Co, 27·70 ; Cl, 32·29. Calculated values for the formula $CoCl_2$ $C_4H_8O_2$: Co, 27·10 ; Cl, 32·56.]

The filtrate, even after keeping at 0° C. or at — 20° C. for several days, did not yield any crystals. After several trial experiments, the following procedure was found to be effective in obtaining a crystalline product from the solution.

The solution (about 50 ml.) was mixed with 100 ml. petroleum ether, thoroughly shaken and allowed to stand. The liquid separated into two layers ; a top colourless layer and a bottom bluish layer of about 10 ml. The bottom layer was separated and washed several times with petroleum ether. The deep-blue solution (about 8 ml.) was freed from traces of petroleum ether and kept at 0° C. Rod-shaped crystals, which got deposited, were removed and washed with petroleum ether. The crystals now had a pale pink or lavender colour. In two to three days, the lavender colour changed to pinkish-grey. [Found : (Per cent.) Co, 27·62 ; Cl, 32·15.] These values closely agree for the formula $CoCl_2$ $C_4H_8O_2$.

The monodioxanate is hygroscopic, becoming wet and pink on exposure to air. It is readily soluble in water and gives a pink solution. When heated in a melting-point tube, colourless vapours are seen to escape at about 150° C. On further heating, the colour fades to ash-grey but no charring occurs. The dioxanate is found to be quite stable when evacuated at 1 mm. pressure. A known weight of the dioxanate when evacuated in a drying pistol at 64° C. lost only 3 per cent. in weight and at 110° C. only 5 per cent., in three hours.

The monodioxanate was found to be highly soluble in absolute alcohol giving an intense blue solution. When dry ether was added to a concentrated solution of the dioxanate in alcohol, slight turbidity and deposition of crystals on the sides of the vessel was noticed. When this solution was left overnight at 0° C. crystals in good yield were obtained. The crystals were separated, washed several times with petroleum ether and kept in a current of dry air for 30 minutes. The product obtained was pinkish-violet in colour. [Found : (Per cent.) Co, 34·22 ; Cl, 41·45. Calculated for the formula $(2\,CoCl_2)$ $C_4H_8O_2$: Co, 33·91 ; Cl, 40·80.]

This violet-coloured dioxanate was found to be very stable when evacuated at 1 mm. pressure and 64° C. the loss in weight being less than 2 per cent. after two hours. At 110° C. a loss in weight of about 12 per cent. was recorded in two hours, with change in colour to bluish-pink.

Nickel chloride dioxanate.—Nickel chloride monodioxanate was prepared in the same way as described before, by treating dry nickel hydroxide suspended in dioxane with hydrogen chloride gas. The product was obtained as a pale yellow powder. [Found : (Per cent.) Ni, 27·58 ; Cl, 32·04. Calculated for the formula $NiCl_2$ $C_4H_8O_2$: Ni, 27·06 ; Cl, 32·56.]

It was not possible to obtain the dioxanate in a crystalline form from the filtrate of the reaction mixture by addition of ether. Although the solution could be concentrated by this procedure and crystals obtained by cooling the solution, it was not possible to free the crystals completely from the mother liquor by washing with petroleum ether. The crystals were wet and greenish and did not give consistent analytical values.

Like the cobalt salt, nickel chloride monodioxanate is hygroscopic, turning wet and green on exposure to air. When heated in a melting-point tube, the colour changed to pale yellow, with escape of vapours at about 190° C. No further changes were noticed till 320° C. A known weight of the dioxanate was evacuated in a drying pistol at 64° C. and there was no loss in weight after two hours. When evacuated at 110° C. it lost only 7 per cent. in weight in three hours.

The lower dioxanate was isolated as a greenish-yellow powder by addition of ether to an alcoholic solution of the monodioxanate. [Found: (Per cent.) Ni, 34·51 ; Cl, 40·44. Calculated for the formula ($2\,NiCl_2$) $C_4H_8O_2$: Ni, 33·90 ; Cl, 40·80.]

This lower dioxanate was found to be similar in its properties to the monodioxanate.

Summary

Monodioxanates of the chlorides of cobalt (ii) and nickel (ii) have been prepared by making hydrogen chloride gas to react with the dry hydroxides, suspended in dioxane. The stability and general characteristics of these dioxanates are recorded. Lower dioxanates, with metal halide to dioxane ratio as 2 : 1, have been isolated from the alcoholic solutions of the monodioxanates.

REFERENCES

1. Rheindboldt, H. *et al.* .. *J. Prakt. Chem.*, 1937, **148**, 81. *Ibid.*, 1937, **149**, 30.
2. Juhaz, R. and Yntema, L. F. *J. Amer. Chem. Soc.*, 1940, **62**, 3522.
3. Crenshaw, J. L. *et al.* .. *Ibid.*, 1938, **60**, 2308.
4. Kelley, C. J. and McCusker, P. A. *Ibid.*, 1943, **65**, 1307.
5. McCusker, P. A. *et al.* .. *Ibid.*, 1959, **81**, 1974 and 2976.
6. Sisler, H. H. *et al.* .. *Ibid.*, 1953, **75**, 2881.
7. Mezhennyi, Y. F. .. *J. Gem. Chem.* (*U.S.S.R.*), 1944, **16**, 447.
8. Sheka, I. A. and Karlysheva, K. F. *Ibid.*, 1951, **21**, 833.
9. Moosath, S. S. and Rao, M. R. A. *Proc. Ind. Acad. Sci.*, 1956, **43**, 213.
10. Nair, S. G. K. and Moosath, S. S. *Ibid.*, 1958, **47**, 344.
11. ———— .. *Ibid.*, 1959, **50**, 337.
12. Moosath, S. S. *et al.* .. Unpublished work on thorium and titanium tetrachloride dioxanates.

dl- MARINDININ (DIHYDROKAWAIN) AND SOME RELATED 6-ARYL-5, 6-DIHYDRO-4-METHOXY-2-PYRONES[1]

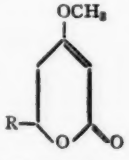
BY K. VISWANATHAN AND S. SWAMINATHAN

(*Department of Organic Chemistry, University of Madras, Madras-25*)

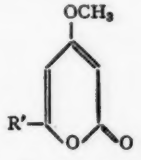
Received March 24, 1960

(Communicated by Dr. K. N. Menon, F.A.SC.)

THE plant kawa kawa (*Piper methysticum*) has been used[2a, b] from ancient times to prepare a narcotic beverage by inhabitants of the South Pacific Islands. Its chemical examination, especially by Borsche and Co-workers,[3] has led to the isolation of several crystalline constituents which include kawain (I), dihydrokawain (II), methysticin (III), dihydromethysticin (IV) and yangonin (V). A pharmacological examination by Van Veen,[4] reported in 1939, indicated the active constituent to be II, referred to by him as marindinin. During the course of the present work, other reports[5–7] of pharmacological screening of the constituents of kawa kawa for central nervous system activity have appeared and these indicate that methysticin (III) and dihydromethysticin (IV) are the most active. The syntheses of all the constituents except II have been reported.[8–12]



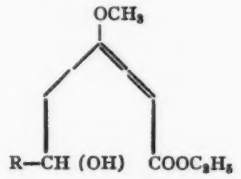
I, R = Styryl
II, R = β-Phenylethyl
III, R = 3, 4-Methylenedioxystyryl
IV, R = β-(3, 4-Methylenedioxyphenyl) ethyl
VII, R = Phenyl
VIII, R = 3, 4-Methylenedioxyphenyl
IX, R = *p*-Anisyl
X, R = α-Naphthyl



V, R' = *p*-anisyl
XI, R' = 3, 4-Methylenedioxyphenyl
XII, R' = Styryl or β-Pyridyl

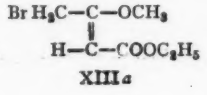
At the commencement of the present study the only published report on the pharmacological examination of kawa kawa was that of Van Veen[4] and it was of interest to prepare racemic marindinin for pharmacological

evaluation in view of the reported activity of the naturally occurring dextro form. *dl*-Kawain was prepared by the method of Kostermans[9] involving the Reformatsky reaction of cinnamaldehyde with ethyl-γ-bromo-β-methoxy crotonate. The use of zinc in the form of dust and longer periods of reaction furnished an improved yield (33·5%). Catalytic reduction of *dl*-kawain with palladised charcoal afforded *dl*-marindinin in 57·5% yield. Prolonged periods of hydrogenation gave acidic products probably resulting from the cleavage of the pyrone ring. The Reformatsky reaction of hydro-cinnamaldehyde directly with ethyl-γ-bromo-β-methoxy-crotonate was also studied. The reaction mixture, when worked up, yielded an oil which when chromatographed on alumina furnished *dl*-marindinin but only in 8·6% yield. This poor yield is probably due to the greater tendency of the intermediate VI *a* as compared to VI *b* to lose water than to cyclise by loss of ethanol. *dl*-Marindinin is a colourless crystalline compound m.p. 72–73° and is virtually identical in infra-red and ultraviolet absorptions with a sample of *d*-marindinin (reported m.p. of the latter 56–58°[3b], 60°[4]).

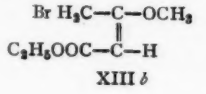


VI *a*, R = β-Phenylethyl
VI *b*, R = Styryl

It was then considered of interest to prepare some analogues of marindinin and the synthesis of some 6-aryl-4-methoxy-5, 6-dihydro-2-pyrones was undertaken in the first instance. The Reformatsky reactions of benzaldehyde, piperonal, *p*-anisaldehyde and α-naphthaldehyde gave 6-phenyl (VII), 6-piperonyl (VIII), 6-*p*-anisyl (IX) and 6-α-naphthyl (X)-4-methoxy-5, 6-dihydro-2-pyrones respectively. The yields of the dihydropyrones ranged from 23–31% except in the case of 6-piperonyl derivative (VIII) which was obtained in 55% yield. The unsatisfactory yields of 5, 6-dihydropyrones in such Reformatsky reactions may be due to the fact that ethyl γ-bromo-β-methoxy-crotonate employed by us and also by previous workers[9, 12, 13] is a mixture of the geometric form XIII *a* with the form XIII *b*. Only the latter can give rise to a Reformatsky product capable of undergoing cyclisation.



XIII *a*



XIII *b*

The availability of 6-substituted-5, 6-dihydro-4-methoxy-2-pyrones presents an attractive approach to the synthesis of the naturally occurring pyrone 4-methoxy paracotoin[14, 15] (XI), not hitherto synthesised and also to other similar pyrones (XII).[14, 15] Studies on the dehydrogenation of the 5, 6-dihydro-4-methoxy-2-pyrones as well as the synthesis of other types of analogues of marindinin are in progress.

Experimental

Ethyl-γ-Bromo-β-Methoxy-crotonate (XIII)

Ethyl-β-methoxy-crotonate was prepared and brominated essentially according to the method of Kostermans[9] to give XIII. For large-scale preparations of ethyl β-methoxy-crotonate, the following method based on that of Michael[16] and not involving large amounts of diazomethane was preferred.

To a well-cooled mixture of ethyl acetoacetate (80 g.) and methyl ortho-formate (70 g.) was added concentrated sulphuric acid (1·5 ml.). The mixture was kept in an ice-chest for 24 hours and then at room temperature for an additional 24 hours. Excess anhydrous potassium carbonate was added, the mixture filtered and freed of unreacted methyl ortho-formate *in vacuo*. The residue was taken up in ether (200 ml.) and washed three times with 2 N sodium hydroxide solution (75 ml.) and then with water. After drying, the ether was removed and the residue distilled. The fraction, b.p. 178–96°, was collected and refractionated to give 25 g. of material, b.p. 186–92°.

General Procedure

6-*Aryl*-5, 6-*Dihydro*-4-*Methoxy*-2-*Pyrones*

A mixture of 0·05 mole of the freshly distilled aldehyde, 0·05 mole of ethyl γ-bromo-β-methoxy-crotonate and 0·05 g.at. of purified zinc dust in 80 ml. of dry benzene was taken in a 250 ml. 3-necked flask fitted with a condenser and mercury sealed stirrer. The reaction was initiated by warming the mixture gently on the water-bath and, if necessary, by adding a pinch of iodine. After allowing the initial reaction to subside, the mixture was refluxed on the water-bath for 3½ hours. The brown reaction mixture was then cooled, decomposed with saturated ammonium chloride solution and the benzene layer separated. The aqueous layer was re-extracted with benzene and the combined layers were washed with water and dried over anhydrous magnesium sulphate. Removal of the solvent gave a residue which when diluted with 5–10 ml. of ether and allowed to stand in the ice-chest for a few hours, deposited yellow crystals. The crystals were collected and crystallised from ethanol to give the colourless products.

TABLE I

Lists the serveral pyrones thus prepared and some of their properties

Aldehyde	Product	M.P.	Yield (%)	Formula	Calculated		Found		I.R. Absorptions $\lambda_{max.}^{CHCl_3, \mu}$	U.V. Absorptions $\lambda_{max.}^{EtoH}$ mμ ($\log_{10}\epsilon$)
					% C	% H	%C	% H		
Cinnamaldehyde	I	145–46°	33·5	$C_{14}H_{14}O_3$	73·0	6·1	73·2	6·3	5·86, 6·13	244 (4·44), 281 (3·19), 291 (3·04)
Hydrocinnamaldehyde ..	II*	72–73°	8·6	$C_{14}H_{16}O_3$	72·4	7·0	72·3	7·1	5·87, 6·13	234 (4·08)
Benzaldehyde ..	VII[17, 18]	143–44°	31·0	$C_{12}H_{12}O_3$	70·6	5·9	70·5	5·7	5·87, 6·18	235 (4·08)
Piperonal ..	VIII	158–59°	54·5	$C_{13}H_{12}O_5$	62·9	4·8	62·7	4·8	5·87, 6·18	238 (4·09)
p-Anisaldehyde ..	IX	95–96°	31·0	$C_{13}H_{14}O_4$	66·7	6·0	66·9	5·9	5·87, 6·18	229 (4·26)
α-Naphthaldehyde	X	154–55°	26·0	$C_{16}H_{14}O_3$	75·6	5·5	75·1	5·7	5·83, 6·12	282 (4·01)

* The crude Reformatsky product was chromatographed as described elsewhere in the experimental section.

dl-*Marindinin* (dl-*Dihydrokawain*) (*II*)

(*a*) *From Hydrocinnamaldehyde.*—The crude Reformatsky product from this aldehyde was a liquid which was chromatographed over alumina. Elution with a 7 : 3 mixture of ether-petroleum ether (b.p. 60–80°) furnished product m.p. 68–70° C. Two crystallisations from ether yielded pure *dl*-marindinin, m.p. 72–73°, yield 8·6%.

(*b*) *By Reduction of Kawain* (*I*).—A suspension of 1 g. of *dl*-kawain in 50 ml. of methanol was hydrogenated over 30% palladium on charcoal at 50 p.s.i. for 12 minutes. The catalyst was filtered off and the filtrate freed of solvent. The residual liquid was taken up in ether and acidic impurities removed by washing the ether solution with 5% sodium bicarbonate solution. Removal of ether afforded a liquid which solidified when cooled. Two crystallisations from ether yielded 0·58 g. (57·5%) of colourless crystals m.p. 72–73° undepressed by and having identical U.V. and I.R. absorptions with product obtained in (*a*).

Summary

Some 6-substituted-5, 6-dihydro-4-methoxy-2-pyrones including the racemic form of marindinin, reported to be an active sedative principle of piper methysticum are described.

Acknowledgements

We are grateful to Dr. J. W. Hinman, Department of Biochemistry, UpJohn Co., Kalamazoo, Michigan, U.S.A., for stimulating our interest in the present study, for generous gifts of chemicals and for providing us most of the analytical data. We are also thankful to Dr. T. R. Govindachari for providing us some of the I.R. data.

References

1. This work is abstracted from the M.Sc. Thesis of K. Viswanathan, submitted in August 1959 to the University of Madras.
2 (*a*) Hough .. *Smithsonian Miscellaneous Collections*, 1904, **47**, 85.
(*b*) Van Veen .. *Geneeskundig Tijdschr. Nederland, Indie*, 1938, **78**, 1941.
3 (*a*) Borsche and Lewinsohn .. *Ber.*, 1933, **66**, 1792 and references to earlier papers therein.
(*b*) Borsche and Peitzsch .. *Ibid.*, 1930, **63**, 2414.
4. Van Veen .. *Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 521.
5. Klohs, Keller, Williams, Toekes and Cronheim *J. Med. and Pharm. Chem.*, 1959, **1**, 95.
6. Hansel and Beiersdorff .. *Naturwissenschaften*, 1958, **45**, 573.
7. Scheuer and Horigan .. *Nature, Suppl.* 13, 1959, **184**, 979.

8. Borsche and Bodenstein .. *Ber.*, 1929, **62,** 2515.
9. Kostermans .. *Rec. Trav. Chim. Pays-Bas*, 1951, **70,** 79.
10. Fowler and Henbest .. *J. Chem. Soc.*, 1950, 3642.
11. Chemielewska, Cieslak, Gorczynska, Kontnik and Pitakowska *Tetrahedron*, 1958, **4,** 36.
12. Klohs, Keller and Williams *J. Org. Chem.*, 1959, **24,** 1829.
13. Kogl and de Bruin .. *Rec. Trav. Chim. Pays-Bas*, 1950, **69,** 729.
14. Mors, Gottlieb and Djerassi *J. Am. Chem. Soc.*, 1957, **79,** 4507.
15. Gottlieb and Mors .. *J. Org. Chem.*, 1959, **24,** 17.
16. Michael .. *J. Am. Chem. Soc.*, 1935, **57,** 159.
17. Henbest and Jones .. *J. Chem. Soc.*, 1950, 3628.
18. Reid and Ruby .. *J. Am. Chem. Soc.*, 1951, **73,** 1054.

A CRITICAL APPRAISAL OF SOME COSMIC RAY DATA FOR THE I.G.Y.

By R. P. Kane

(Physical Research Laboratory, Ahmedabad-9)

Received May 13, 1960

(Communicated by Prof. V. A. Sarabhai, F.A.SC.)

Abstract

Cosmic ray recordings made with comparable instruments at stations where one would expect similar responses to primary variations of intensity have been examined. Discrepancies of the order of a few per cent. are sometimes observed. The discrepancies are often too large to be explained either on the basis of statistical errors or through the application of improper meteorological corrections.

The order of magnitude of the discrepancies in intensity averaged on a bi-hourly, 6-hourly and 24-hourly basis is evaluated. The validity of drawing conclusions of physical significance from the I.G.Y. data under various conditions is discussed. The importance of applying appropriate statistical tests to available data is emphasised.

I. Introduction

The study of the variations of cosmic ray intensity has been carried on for the past two decades at various places in the world. An effort was made during the recent I.G.Y. period (June 1957 to December 1958) to operate standard cosmic ray measuring instruments in different parts of the world on a continuous basis. The work has been pursued with great enthusiasm with the result that neutron monitors and cosmic ray meson telescopes have operated at more than 50 places during the I.G.Y. period and many of these have undertaken to continue this effort for one more year for the so-called I.G.C. period (January to December 1959).

Recently, an attempt was made by us to use the data from some of the stations for the purpose of studying the latitude and longitude effects of cosmic ray time variations. The analysis revealed some striking effects. For example, one could see that on a bi-hourly basis some stations in the northern hemisphere showed differences of intensity as large as 5% when

compared with some of the southern stations. The implication of the observation, if genuine, would be very important. It was felt necessary, therefore, to confirm whether the basic data utilised for this analysis were free from instrumental faults.

Although, most of the stations run duplicate sets of recording units, data submitted to the W.D.C. are usually combined for the two sides. There is no way, therefore, to judge from the data sheet whether the data are suspect unless the authors give comments to indicate faulty data. One can, however, approach the problem from a different point of view and ask the question: Do stations situated very near each other, say within 100 miles of each other and at similar elevations, indicate a parallel running of cosmic ray intensity recordings made with similar instruments ?

With a view to check the reliability of cosmic ray recordings on this basis, an attempt was made to pick out groups of stations which had roughly the same location and altitude and hence were expected to depict similar variations of cosmic ray intensity within statistical errors. Unfortunately, amongst the stations directly operated by the Physical Research Laboratory, Ahmedabad, India, one does not have any two which can be used for the present purpose. An attempt was made, therefore, to look for such groups at other places in the world. The data were obtained from the recent publication[1] *Cosmic Ray Intensity during the International Geophysical Year, No.* 1 published by National Committee for the I.G.Y., Science Council of Japan, Ueno Park, Tokyo, Japan, 1959.

II. Comparison of British Stations

The stations at London, Leeds and Herstmonceux are located very near one other and have provided neutron monitor data for the I.G.Y. period. Table I gives the details of the location of the three stations as also of the data they provide.

TABLE I

Details of the British stations at Leeds, London and Herstmonceux

	Geographic		Alt.	Cut-off energy BeV	Bi-hourly std. error %	Barometric coefficient used %/mb.
	Lat.	Long.				
Leeds ..	.. 53° 49′ N	1° 33′ W	100 m.	1·6	·54	·68
London	.. 51° 32′ N	0° 06′ W	SL	2·1	·41	·72
Herstmonceux	.. 50° 52′ N	0° 20′ E	23 m.	2·2	·34	·77

Figure 1 is a plot of the difference between the % bi-hourly values of the three pairs of stations. The mean value of the difference is indicated by a horizontal line and on either side of this line two more lines are marked at

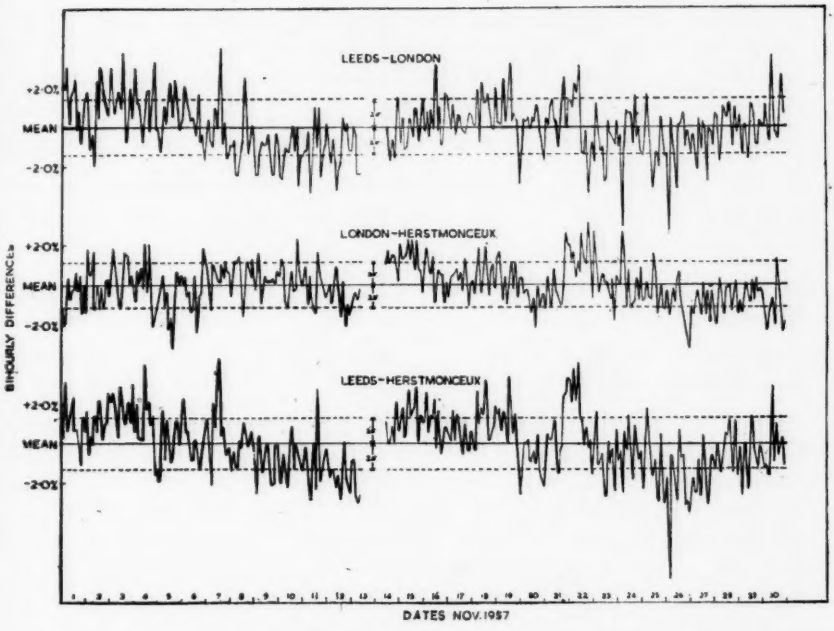


FIG. 1. Bi-hourly percentage differences, Leeds *minus* London, London *minus* Herstmonceux and Leeds *minus* Herstmonceux.

distances $\pm 2\sigma$ where σ represents the standard error of the bi-hourly difference, computed from the theoretical value to be expected from a Poisson distribution.

On purely statistical considerations, one would expect that 95% of the differences in bi-hourly percentage values would lie within the $\pm 2\sigma$ limits indicated in Fig. 1. Table II gives a comparison of the number of expected and observed values exceeding $\pm 2\sigma$ limits.

It is clear from Fig. 1 and Table II that there are two types of discrepancies present in the data. Firstly, the differences in the bi-hourly values are not randomly scattered in the $\pm 2\sigma$ limit. For several consecutive values, the deviations lie either above or below the zero line. Such a pattern is strongly suggestive of systematic errors in the basic data. Secondly, the number of

TABLE II

Comparison of the number of bi-hourly deviations exceeding ± 2σ limits actually observed and those expected by statistics

Stations	Series 1 (Nov. 1–13, 1957)			Series 2 (Nov. 14–30, 1957)		
	Total No. of bi-hourly values	Values outside ±2σ		Total No. of bi-hourly values	Values outside ±2σ	
		Expected	Observed		Expected	Observed
Leeds *minus* London	150	8	51	198	10	38
London *minus* Herstmonceux	150	8	37	198	10	60
Leeds *minus* Herstmonceux	150	8	52	198	10	78

observed deviations exceeding the $\pm 2\sigma$ limits is many times larger than the number expected from statistical considerations. In the present case where three stations are available for consideration, one can examine individual bi-hourly values and see whether one can spot out as suspect the bi-hourly value of any one station at a time. It was found that this could be done satisfactorily and it was necessary to discard 115 bi-hourly values at one or other of the three stations, out of a total of 348 values.

III. COMPARISON OF PAIRS OF STATIONS

From the previous section, it can be seen how useful it is to have comparable data for three near-by stations. It is rather unfortunate that from the grid of I.G.Y. stations operating neutron monitors, one cannot select any other group of three or more adjoining stations which can be directly compared. However, it is possible to select a few *pairs* of stations operating neutron monitors during I.G.Y. We have confined our attention only to neutron monitors and have not considered meson telescopes, because the meteorological corrections are more precisely known for the nucleonic component than for the meson component of cosmic ray intensity. The pairs of stations selected are indicated in Table III.

An analysis similar to that made for the pairs of British stations was carried out for each of the pairs mentioned in Table III for the period July

TABLE III

Details of pairs of stations selected from the I.G.Y. grid of neutron monitors

Pair	Geographic		Altitude (metres)	Cut-off energy (BeV)	Bi-hourly std. dev. %	Barometric coefficient %/mb. Hg
	Lat.	Long.				
(1) Resolute ..	74° 41′ N	94° 54′ W	17	0	·52	·73
Thule ..	76° 33′ N	68° 50′ W	SL	0	·50	·74
(2) Ottawa- ..	45° 24′ N	75° 54′ W	101	1·7	·53	·72
Deep River	46° 06′ N	70° 30′ W	145	1·3	·48	·71
(3) Lincoln ..	40° 49′ N	96° 41′ W	350	2·6	·53	·72
Chicago ..	41° 50′ N	87° 40′ W	SL	2·4	·48	·72
(4) Gottingen ..	51° 31′ N	9° 56′ E	273	2·4	·41	·72
Weissenau	47° 48′ N	9° 30′ E	427	3·2	·43	·78
(5) Pic-du-Midi	42° 56′ N	0° 15′ E	2860	3·9	·17	·75
Zugspitze ..	47° 25′ N	10° 59′ E	2960	3·3	·15	·79
(6) Huancayo ..	12° 02′ S	75° 20′ W	3400	13·2	·18	·73
Mina Aguilar	23° 12′ S	65° 42′ W	4000	11·8	·15	·71

to December 1957. Table IV gives the total number of bi-hourly values exceeding $\pm 2\sigma$ limits during the six-month period July to December 1957, for the various pairs of stations.

It can be seen from Table IV that the number of observed bi-hourly deviations exceeds the number expected from statistical considerations by a factor of about 5. The pair Ottawa-Deep River seems to have the least fraction of discrepancies.

IV. Possible Causes of Differences Between Neighbouring Stations

It is clear from the above analysis that the discrepancies observed cannot be explained as random errors. We examine below other causes which could give rise to differences between neighbouring stations.

(*i*) *Method of presentation of data.*—For the present analysis, data as given in the publication *Cosmic Ray Intensity during the I.G.Y., No.* 1 are used. The data are in the form of natural logarithms except for the stations of Pic-du-Midi and Weissenau for which data are presented in the usual form, *viz.*,

TABLE IV

Number of bi-hourly values exceeding ± 2 σ limits for various pairs of stations for the period July–December 1957

Pair	Total No. of bi-hourly values	Values outside ± 2σ		Ratio of Observed to Expected values
		Expected	Observed	
(1) Resolute .. .. Thule	1457	73	362	5·0
(2) Ottawa- .. .. Deep River	1546	77	236	3·1
(3) Lincoln .. .. Chicago	1864	93	390	4·2
(4) Gottingen .. .. Weissenau	2136	107	540	5·1
(5) Pic-du-Midi .. Zugspitze	1419	71	748	10·5
(6) Huancayo .. .. Mina Aguilar	1014	51	259	5·1
(7) Leeds .. .. London	1460	73	412	5·6
(8) Leeds .. .. Herstmonceux ..	2111	106	737	7·0
(9) London .. .. Herstmonceux	1488	74	521	7·0

percentage deviations from an arbitrarily chosen fixed mean bi-hourly counting rate, for some months. However, in the publication mentioned above, the editors have pointed out on page V that there is a negligible difference between the two scales when the variations are of a few per cent. To estimate the magnitude of the differences involved, the data for the Chicago neutron pile, which were kindly provided to us by the original investigators directly, were compared with the same data presented logarithmically in the Japanese publication. It was found that the two agreed with each other within 0·2%.

(*ii*) *Meteorological corrections.*—Since the data chosen are for neutron monitors only, the only meteorological correction needed is the barometric

correction. Usually, a linear pressure correction is applied to the normal cosmic ray percentage deviations from a fixed mean, using a pressure coefficient of 0·72 %/mb. Hg. As pointed out by Dorman *et al.*,[2] a discrepancy can arise if the second and higher order terms in pressure are neglected. If however, data are represented logarithmically[3] before applying pressure correction, these discrepancies can be avoided.

Unfortunately, the data used in the present analysis are not corrected for barometric pressure in the way envisaged in the logarithmic representation method. Since many investigators send their data already corrected for barometric effect by applying the usual linear correction, the editors have only converted the pressure corrected bi-hourly counts into their natural logarithms for most of the stations. It is clear, therefore, that though the majority of the data are presented as logarithms of the number of counts, the pressure corrections applied are not free from the discrepancies that can occur if second and higher order terms in pressure are neglected. In addition, it will be seen from Tables I and III that the pressure coefficients used for the data at various stations are not constant but vary from about 0·70 to 0·80 % per mb. Hg.

The discrepancies occurring in the data because of these non-uniformities in pressure correction are expected to be of the order of 0·1 %/mb. Hg. However, to explain differences of the order of 2% or more between near-by stations, one would require to assume that pressure differences as high as 10–15 mb. occur between these stations within a period of two hours. Such changes may occur during great storms. But they are certainly not so frequent as to affect 30% of the bi-hourly values.

(*iii*) *Difference in location of stations in a pair.*—As has been mentioned in the beginning, the stations in any pair are chosen so as to have approximately the same latitudes, longitudes and altitudes. In Tables I and III, the cut-off energies of the primary cosmic rays arriving at each station are given. It will be seen that for any pair, the values hardly differ by more than one BeV. To produce changes of the order of 2% between the two stations, one will have to assume a very steep primary energy spectrum of variations. This is highly improbable, though not impossible. If such changes do occur, they will disturb greatly the general pattern of the latitude dependence of cosmic ray intensity.

(*iv*) *Differences due to faulty data.*—The discrepancies may be due to faulty basic data. These can be located by a comparison of data from two similar instruments kept adjacent to each other but operated independently.

The statistical method adopted for checking their parallel running would be similar to the one outlined earlier in this paper for two near-by stations. From our own experience with the data obtained at the stations at Kodaikanal and Ahmedabad, we find that such checks are very essential for sorting out reliable data. After applying statistical checks, we have had to reject data for many bi-hours at both the stations. We have also examined the data for the two sections of the neutron monitor operated at Huancayo, which were available to us by the kind courtesy of the original investigators. On examining the differences of bi-hourly values for the two sides for the month of May 1958, it was found that the number of values exceeding the $\pm 2\sigma$ limits was about twice the number expected from statistical considerations. This seems to indicate that discrepancies are likely to be present in the basic data.

V. MAGNITUDE OF DISCREPANCIES

Knowing that these discrepancies are outside statistical errors and are not caused by any peculiarities of processing of data or differences in meteorological corrections, it is worthwhile estimating the extent to which these effects of the total number of bi-hourly, 6-hourly and 24-hourly mean values during the six-monthly period July–December 1957 is showing discrepancies exceeding 2% when percentage values of pairs of stations are compared. These values are given in Table V.

It is clear from Table V that a considerable fraction of the bi-hourly values for most of the pairs shows discrepancies greater than 2%. For 6-hourly values, the position improves slightly. It is much better for the daily means. One may also view these discrepancies as an enhanced standard error of the basic data.* Thus, one could calculate the experimental standard error σ applicable to each pair of stations so that 95% of the deviations lie within $\pm 2\sigma$ limits. The statistical and experimental standard errors are given in the last two columns of Table V. It will be seen that the experimental standard errors are almost double the statistical standard errors. Recently, McCracken[4] and Dyring[5] have shown that for various instrumental reasons, the statistical distribution followed by the nucleonic component measured by a standard neutron monitor is not exactly Poisson but is roughly Normal with a standard error of $\pm 1{\cdot}2\sqrt{N}$ where N is the mean counting rate. However, the present analysis shows that the standard error is as high as $2\sqrt{N}$ in several cases, which is strongly indicative of faulty basic data.

* Suggestion by Prof. Morrison which is gratefully acknowledged.

TABLE V

Fraction of the total number of bi-hourly, 6-hourly and 24-hourly values showing discrepancies exceeding 2% for the various pairs

Pair	Fraction of values showing discrepancies exceeding 2%			Percentage std. error of bi-hourly differences	
	Bi-hourly values %	6-hr. values %	24-hr. values %	Statistical	Experimental
(1) Resolute .. .. Thule	10·6	2·7	0·0	·72	1·25
(2) Ottawa- .. .. Deep River	4·1	0·4	0·0	·72	0·95
(3) Lincoln .. .. Chicago	7·7	0·8	0·0	·72	1·15
(4) Gottingen .. .. Weissenau	6·2	3·1	0·0	·59	1·05
(5) Pic-du-Midi .. Zugspitze	11·4	11·7	7·3	·23	1·35
(6) Huancayo .. .. Mina Aguliar ..	0·2	0·0	0·0	·23	0·50
(7) Leeds .. .. London	14·4	6·5	1·4	·68	1·40
(8) Leeds .. .. Herstmonceux	20·3	13·4	9·0	·64	1·65
(9) London .. .. Herstmonceux	10·9	5·3	0·0	·53	1·25

These discrepancies put a restriction on the type of analysis that can be undertaken with the use of the abovementioned data. For effects involving variations of the order of 5–10%, the present discrepancies are not likely to matter. For example, large Forbush type decreases will easily be detectable in spite of the faults in the data. However, during comparison of finer details of such changes, for example, the exact onset times of the Forbush decreases as also the precise latitude dependance of the magnitude of a Forbush decrease,

the accuracy of the basic data is required to be better than 1%. In such cases, the present I.G.Y. data will need thorough scrutiny before analysis.

The present discrepancies will matter most in the study of variations like the daily variation of cosmic ray intensity where the effects observed are of the order of 1 or 2% and discrepancies of the same order in the basic data could not be tolerated. As seen from Table V, appreciable fraction of the bi-hourly values have inherent discrepancies of about 2%. Therefore, unless methods are employed to spot out faulty values and discard them or manipulate them on some reasonable grounds, it would be unsafe to use the bi-hourly data for study of the day-to-day changes in the nature of the daily variation.

VI. CONCLUSION

It seems from the present analysis that discrepancies of the order of 2% are inherently present in the basic data of some of the neutron monitor stations operated during the I.G.Y. These are likely to affect greatly the conclusions that could be drawn regarding variations in cosmic ray intensity of the order of a few per cent. It seems necessary, therefore, that before any analysis of the I.G.Y. data is undertaken, the following checks should be applied:—

(1) Adjacent neutron monitors at the same station should be first tested for parallel running. This becomes easier if there are three or more instruments for intercomparison. However, even in case of only two instruments, when a certain bi-hourly difference exceeds the $\pm 2\sigma$ limit, one can see which of the two bi-hourly values is abnormally higher or lower than its preceding and succeeding bi-hourly values. It is found that with such an inspection it is possible to locate the faulty bi-hourly value in most of the cases. After identifying the faulty value, it can be discarded and the mean of the preceding and succeeding bi-hourly values substituted in its place.

It should be noted, however, that adjusting values exceeding $\pm 2\sigma$ limits does not necessarily remove all faults in the data. As mentioned earlier, there can be systematic errors within $\pm 2\sigma$ limits also. Thus, the counting rate of one section may be higher or lower than that of the other section for a limited period and then the difference in level may change. It is difficult to prescribe general methods of correction for such systematic errors. These should be dealt with and corrected for individually.

(2) The combined data so obtained for any station should be compared with the data of one or more stations situated near-by. Data showing discrepancies should be discarded.

(3) On comparing data of one group of stations with another group and finding a significant difference of some magnitude, it should be confirmed that various stations in the same group do not show between themselves variations of the same order of magnitude.

These and similar other checks, though trivial looking, are very important for any analysis and should be given due attention by any worker who aims at a study of the precise nature of effects which are expected to be rather small in magnitude. All data from the experimental programme operated by the Physical Research Laboratory are checked in this way. It is hoped that similar checks would be applied as a standard practice at all cosmic ray stations.

Thanks are due to the various research groups and their sponsoring authorities by whose effort the data utilised in this analysis were obtained.

The author is grateful to Dr. V. A. Sarabhai for helpful discussions and criticism. Thanks are due to Mr. S. R. Thakore and others for computational assistance and to the Atomic Energy Commission of India for financial assistance.

References

1. *Cosmic Ray Intensity during the International Geophysical Year—No.* 1, published by National Committee for the I.G.Y. Science Council of Japan, Ueno Park, Tokyo, Japan, 1959.

2. Dorman, L. I., Glokova, E. S. and Kaminer, N. S. — *Instructions of the Introduction of Meteorological Corrections into Data of Cosmic Ray Intensity.* Translation of *Res. Inst. of Terr. Mag., Ion and Radio Wave Prop.*, 1958, p. 6.

3. Wada, M. .. *J. Sci. Res. Inst.*, 1957, **51**, 201.

4. McCracken, K. G. .. *Thesis*, University of Tasmania, 1958.

5. Dyring, E. .. *Statistical Studies of the Performance of Cosmic Ray Recording Instruments* (in preparation), 1960.

STUDIES ON COLLAGEN

VI. Influence of Lyotropic Salt Solutions on the Optical Activity of Collagen

BY S. VENKATARAMAN

(Department of Physics, University of Madras, Madras-25, India)

Received July 19, 1960

(Communicated by Dr. G. N. Ramachandran, F.A.SC.)

1. INTRODUCTION

STUDIES on the effect of lyotropic salt solutions on collagen fibres were made in this laboratory by X-ray diffraction methods (Santhanam, 1959). From the disappearance of the spots characteristic of the fibre it was concluded that the structure must be disorganised after the chemical treatment. But since the original pattern could be restored by washing the fibre with water, it is clear that the changes brought about by the salt solutions must be purely structural in character. Also since the X-ray pattern of a chemically shrunk collagen fibre in its final state is very similar to that of thermally shrunk collagen, the structural changes taking place in both the cases must be similar.

The effect of thermal degradation on the optical activity of collagen and gelatin has been investigated in detail (Robinson, 1953; Cohen, 1955). The marked lowering of the specific rotation from about $-350°$ to $-110°$ has been attributed to the loss of the "collagen fold" or helix (Robinson, 1953). Boedtker and Doty (1956) have reported a similar lowering of the specific rotation when collagen solution (carp swim-bladder) is treated with 2 M KCNS. The equivalence of the denaturation by 2 M KCNS and by heating to 36·5° C. was shown by measurements of viscosity and light scattering molecular weight. Doty and Nishihara (1958) have found from light scattering measurements on denatured calf skin collagen that the weight average molecular weight of the parent gelatin is the same whether the denaturation is brought about by heating the collagen solution to 40° C. or by treatment with 2 M KCNS. Bradbury *et al.* (1958) have reported lowering of the specific rotation when a solution of rat skin collagen is treated with neutral salts such as KCNS, KI or KBr, and they have also shown that the denaturation is partially reversible; on dialyzing out the salt a rise of specific rotation to about $-250°$ has been observed. But since the studies on thermal degradation have been carried out on collagen from carp swim-bladder (Cohen, 1955),

it was felt desirable for comparison of results that the same material be used in studying the degradation brought about by neutral salts. Also, among such salts $CaCl_2$ is one of the most effective lyotropic agents known, whose effect on the optical activity of collagen has not been previously reported. In this paper studies on the effect of $CaCl_2$, KI and KCNS on the optical activity of collagen from carp swim-bladder are reported. It is found that the specific rotation is lowered to about $-80°$, while the corresponding value for the thermally degraded collagen is only $-110°$. The major part of the lowering is evidently due to the destruction of the characteristic helical structure of collagen; the further lowering of the specific rotation is to be attributed to solvation effects, as shown in the discussion. It may be mentioned that these studies were carried out at intervals during the last three years and were coeval with some of the work reported above.

Also it is known that high acetate ion concentration in acetate buffers causes irreversible denaturation of the protein (Tomlin and Turner, 1957). To avoid this complication the acetate ion concentration was kept low by using 1 M acetic acid as the solvent for collagen. After addition of the lyotropic salt solutions the concentration of the acetic acid was still high (M/3).

2. Experimental

The tunics of fresh carp swim-bladder, after removal of the soluble tissue proteins and carbohydrates, were extracted with cold 1 M acetic acid. The extract was separated from the tissue by filtering through a sintered glass filter at 7° C., which leaves a clear highly viscous filtrate. The filtrate was stored at 7° C. and used directly for experiments. The term ichthyocol refers to this acetic acid extracted material.

The protein concentration was estimated by Nesslerisation, 5·7 times the Nessler nitrogen being the protein concentration, which corresponds to 17·5% nitrogen in the dry solid material as found by Kjeldahl analysis (Gallop, 1955).

Measurements of optical rotation were made with a Hilger Microptic Polarimeter using filtered sodium lamp and 2 dm. tubes. For measuring the rotation of collagen solutions at temperatures below the room temperatures a very simple technique was adopted. The solution was equilibrated at the required temperature overnight, then transferred to the polarimeter tube and the rotation measured at once. It was found by actual experimentation that no change in the optical rotation took place within the time necessary for taking a set of readings, if the collagen solution was not previously subjected to repeated heating and cooling. Consequently elaborate

arrangements connected with the circulation of thermo-regulated water through the jacket of the polarimeter tube, were entirely dispensed with.

Saturated solutions of $CaCl_2$, KI and KCNS were prepared and their concentrations were obtained from tables (*e.g.*, Seidell, 1940). In the case of $CaCl_2$ the salt concentration was also estimated by chemical analysis, by precipitating calcium as oxalate and titrating against standard permanganate. The results were agreeing.

3. RESULTS

Addition of concentrated salt solutions to ichthyocol generally resulted in the precipitation of protein unless the concentration of the salt was fairly high, ca. 3 M or more. The amount of salt solution necessary for holding the protein in solution was found by a preliminary experiment. Measured aliquots of ichthyocol were treated with the salt solutions and kept overnight at 7° C. The rotation of the cold solution was measured as before, and the solution was allowed to warm up to the room temperature (31° C.). There was no further change in the rotation, and even after equilibrating the solution at 40° C. for 1 hr. there was still no change.

The following details pertaining to the treatment of ichthyocol with $CaCl_2$ are typical. At less than 3% w/v. concentration of the salt, the specific rotation was the same as that for pure collagen (— 353°). On increasing the concentration beyond 3% the protein was precipitated. At 30% concentration (2·7 M), the protein was held in solution and the specific rotation was — 94°. At 3·4 M concentration $[\alpha]_D^7$ was — 86°, and on increasing the concentration to 4·0 M there was no further change in the specific rotation. Also on raising the temperature from 7° C. to 31° C., the specific rotation did not change.

(*a*) *Effect on Thermally Degraded Collagen.*—It was noticed that ichthyocol stored at 7° C. for long periods, ca. 2 months, acquired a certain resistance to thermal degradation, in that the specific rotation changed only very slowly on raising the temperature. In fact when the sample of ichthyocol was left at room temperature, the specific rotation decreased very slowly and an equilibrium state was not reached even after two days. To hasten the pace of degradation ichthyocol was kept at 50° C. overnight and cooled to room temperature (31° C.). The specific rotation was found to be steady at — 132°. It was subsequently found that the rotation could be brought down to — 112° by equilibrating the solution at 60° C. overnight. However, the present studies were conducted on the sample for which $[\alpha]_D^7$ was — 353° and $[\alpha]_D^{31}$ was — 132°. The results are given in Table I.

TABLE I

Lyotropic salt	Molar concentration of salt	Specific rotation of treated ichthyocol: Unheated $[\alpha]_D^7$	Heated to 31° C. after treatment $[\alpha]_D^{31}$	Heated to 31° C. before treatment $[\alpha]_D^{31}$
$CaCl_2$	3·4 M	−86°	−86°	−81°
KI	4·8 M	−77°	*	−71°
KCNS	5·2 M	−82°	−82°	−81°

* Rotation could not be measured because the solution developed a brown colour.

(*b*) *Effect of Dilution.*—Chemically treated ichthyocol, using concentrations as in Table I, was diluted with cold distilled water in the ratio 1 : 4. In the solution containing KCNS protein was precipitated at once. In the case of $CaCl_2$ and KI, dilution did not cause precipitation, but the KI solution had to be rejected because it soon developed a brown colour. The diluted collagen solution containing $CaCl_2$ was kept at 7° C. for 17 days. It was found that the specific rotation had increased from −86° to −163°. The solution was further diluted with an equal volume of cold water and kept at 7° C. for 20 days. There was no further increase of the specific rotation. Measurements were also taken with salt concentrations of 2·7 M and 4·0 M, at which the specific rotations were − 94° and − 86° respectively. The results are summarised in Table II.

TABLE II

Concentration of $CaCl_2$	Specific rotation of treated ichthyocol: $[\alpha]_D^7$	$[\alpha]_D^{31}$
0·85 M	−163°	..
2·7 M	− 94°	−94°
3·4 M	− 86°	−86°
4·0 M	− 86°	−86°

(*c*) *Effect of pH.*—pH of the collagen solution was changed by adding suitable quantities of dilute HCl or NaOH solutions. In the pH range 5–10 protein was precipitating, but on raising the pH the precipitate re-dissolved giving a clear solution. After measuring the rotation of these solutions at 7° C., they were kept at 75° C. for 1 hr. so as to hasten the place of degradation, quickly cooled to the room temperature (26° C.), and the rotations again measured. These values may be taken as representing the degraded state because the cooling was quick and the room temperature was not very low. pH of the chemically treated collagen solution containing 3·4 M $CaCl_2$ was also similarly varied and the specific rotation determined at 7° C. But now, no measurement could be made at alkaline pH because of precipitation. The results are listed in Table III. It may be mentioned that Burge and Hynes (1959) have recently reported that variations of pH in the acidic range, pH 1·2 to pH 3·7, have no effect on the optical rotation of collagen solutions. The reduction observed by the author for the thermally degraded collagen at the alkaline pH 11 has not been reported by them.

TABLE III

pH	Specific rotation of ichthyocol		
	Undegraded $[\alpha]_D^7$	Thermally degraded $[\alpha]_D^{26}$	Chemically degraded by $CaCl_2$ $[\alpha]_D^7$
2	−357°	−126°	−81°
3	−357°	−126°	−81°
4	−357°	−126°	−81°
11	−357°	− 92°	..

4. DISCUSSION

It is known from various physical chemical studies (Doty, 1959) that collagen molecules in solution occur as long thin rods with a diameter of about 13 A which corresponds to the triple chain protofibril in the structure. Thus the typical coiled coil structure would be expected to be present even in solution and this is supported by the large negative specific rotation. On the other hand, on heating or on chemical treatment as shown in this paper,

the specific rotation drops to about one-third, *i.e.*, — 100°. The latter corresponds roughly to the rotation exhibited by the uncoiled beta form of the polypeptides, and may therefore be taken to indicate the disruption of the specific triple helix of collagen.

The X-ray diffraction pattern of specimens treated for a long time with lyotropic salt solutions also supports this evidence. Thus, the distribution of intensity in the X-ray pattern in this case as well as that of hot gelatin, is different from that of cold gelatin, showing the breaking down of the triple helical structure (Ramachandran, 1958; Santhanam, 1959).

It is however interesting to note that the specific rotation of the degraded collagen is about —110° to — 130°, which is also the value for hot gelatin, if the degradation is brought about by heating, while it goes down to about — 80° in the three salt solutions. It is an interesting fact that alkaline pH produced a reduction in the specific rotation of the degraded collagen below the normal value of — 110°, similar to what is found at high salt concentrations. Since even if the solutions are heated to a higher temperature, the specific rotation does not fall below — 110°, this further decrease must not be attributed to a further degradation, but rather to solvation effects. Unfortunately, because of protein precipitation, measurements could not be made with strong solutions of other salts which do not have a lyotropic effect. However, such appreciable variations of optical rotation with the solvent used and the pH are quite common in amino-acids and is also found in some polypeptides.

It is a significant fact that lyotropic effect occurs only at high concentrations (Gustavson, 1956), when the solution contains a number of unionised salt molecules. This observation agrees with that of Santhanam on the effect of such salts on the fibres of collagen, namely that the lyotropic effect cannot be attributed to any ion as such, but rather to the whole molecule of the salt. At slightly lower concentrations the lyotropic effect must be less, and consequently the specific rotation must increase. On diluting the collagen solution containing $CaCl_2$ we actually observe such an increase of the specific rotation, as expected. This shows also that the denaturation brought about by the salt solution is reversible.

5. Summary

The present studies on the effect of lyotropic salt solutions on the optical activity of collagen were made with the idea of confirming the observations of Santhanam (Part V of this series) on the similarity between the actions of lyotropic salt solutions and temperature on collagen. It is known from studies on optical activity accompanying thermal degradation of collagen

that the destruction of the characteristic helical structure of collagen leads to a marked lowering of the specific rotation from about $-350°$ to $-110°$. A similar lowering of rotation has been found to occur when collagen dissolved in acetic acid is treated with concentrated solutions of lyotropic neutral salts such as $CaCl_2$, KI and KCNS. These salts reduce the specific rotation from $-350°$ to about $-80°$ when used at concentrations of 3 M or more. The major part of the lowering is evidently due to the destruction of the helical structure; the further lowering of the specific rotation is to be attributed to solvation effects, as shown in this paper. Also, on warming the solutions subsequently, there is no further change in rotation, which indicates clearly that the effect of the chemical reagents is very similar to that of heat. It was also found that denaturation brought about by the salt solution was reversible, for the specific rotation increased on dilution in the case of $CaCl_2$.

ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to Professor G. N. Ramachandran for his keen interest in this work, and to Dr. Y. Nayudamma, Director, Central Leather Research Institute, for the facilities provided at the Institute for carrying out polarimetric work, at the initial stages of the experiment. Thanks are also due to the Council of Scientific and Industrial Research for financial assistance.

REFERENCES

Boedtker, H. and Doty, P. .. *J. Amer. Chem. Soc.*, 1956, **78**, 4267.

Bradbury, E. M., Burge, R. E., Randall, J. T. and Wilkinson, G. R. *Disc. Faraday Soc.*, 1958, **25**, 173.

Burge, R. E. and Hynes, R. D. *J. Mol. Biol.*, 1959, **1**, 155.

Cohen, C. .. *J. Biophys. Biochem. Cytol.*, 1955, **1**, 203.

Doty, P. .. *Rev. Mod. Phys.*, 1959, **31**, 61.

——— and Nishihara, T. .. *In Recent Advances in Gelatin and Glue Research*, Editor: G. Stainsby, Pergamon Press, London, 1958, p. 92.

Gallop, P. M. .. *Arch. Biochem. and Biophys.*, 1955, **54**, 486.

Gustavson, K. H. .. *Chemistry and Reacivtity of Collagen*, Academic Press Inc., New York, 1956, p. 171.

Ramachandran, G. N. .. *In Recent Advances in Gelatin and Glue Research*, Editor: G. Stainsby, Pergamon Press, London, 1958, p. 32.

Robinson, C. .. *In Nature and Structure of Collagen*, Editor: J. T. Randall, Butterworth, London, 1953, p. 96.

Santhanam, M. S. .. *Proc. Ind. Acad. Sci.*, 1959, **49 A**, 215.

Seidell, A. .. *Solubilities of Inorganic and Metal Organic Compounds*, D. Van Nostrand Company, New York, 1940, **1**, 280.

Tomlin, S. G. and Turner, K. J. *Biochem. Biophys. Acta*, 1957, **26**, 170.

A PROBLEM IN PROBABILITY RELATED TO THE PASSAGE OF LIGHT THROUGH A CLOUD OF PARTICLES

By G. N. Ramachandran, F.A.Sc.

(Department of Physics, University of Madras, Guindy, Madras-25)

Received July 23, 1960

1. Introduction

If a beam of light passes through a cloud of opaque spherical particles, containing N particles per unit volume each of cross-sectional area a, then it is readily shown that the variation of intensity I_z with depth z is given by the differential equation

$$dI_z = -NaI_z dz \tag{1}$$

whose solution is

$$I_z = I_0 e^{-Naz}. \tag{2}$$

This corresponds to the so-called geometrical optics case, in which all diffraction effects have been neglected.

It is also possible to work out the above problem by considering the effect of each particle in turn on the energy content of the transmitted beam. This has been done by the author (Ramachandran, 1943. This paper also contains an account of the physical optical approach) and the theory leads to the formula

$$\frac{E_n}{E_0} = \left(1 - \frac{a}{A}\right)^n \tag{3}$$

for the energy content of a beam of cross-sectional area A after it has encountered n particles, each presenting an area a to the beam. Since $n = NAz$ we have from Equation (3)

$$\frac{I_z}{I_0} = \frac{E_z}{E_0} = \left(1 - \frac{a}{A}\right)^{NAz}. \tag{4}$$

It is clear that Equations (2) and (4) are not identical, but that the latter goes over into the former when $a/A \ll 1$. Thus, the exponential formula (2)

is really an approximation valid only when the continuous approximation in Equation (1) is made, although in practical examples, the difference between (3) and (4) cannot be noticed.

The problem of finding the energy content of the beam after it has encountered n particles of cross-sectional area a is identical with one in which n discs, each of area a, is thrown at random over an area A, and it is required to find the probable area covered by the n discs. An essential step in obtaining this is the following. Suppose A_m is the uncovered area after m discs have been thrown and $B_m = (A - A_m)$ is the covered area, then the probable additional area that is covered on throwing the $(m + 1)$th disc is

$$\Delta B_m = \left(\frac{A_m}{A}\right) a. \tag{5}$$

This is obviously true if a, the area of the disc, is small compared with the area A_m, for the probability that its centre occurs in the uncovered area is exactly A_m/A and when it does so, it covers an additional area a, so that the probable additional area that is covered is $(A_m/A)\,a$.

However, the result does not follow so simply if the area of the disc is not small, for the additional area that is obscured will be less than a if its centre lies close to the boundary of a region of the uncovered area A_m and further the $(m + 1)$th particle may cover a portion of the region A_m even if its centre lies outside the region A_m. The calculation of the mean additional area that is covered by the $(m + 1)$th disc would, therefore, appear to be very difficult. However, it is the purpose of this paper to show that Equation (5) is still true under all conditions for the probable (or mean) additional area that is covered and that it is *independent of the size or shape* of both the disc (a) and the aperture (A). This very surprising result follows quite generally from a simple theorem connected with the integral of the *Faltung* or convolution of two functions. In fact the general approach can be used to work out the mean transmission through a cloud of n particles, or discs, when each particle is not only of arbitrary cross-section but exhibits variations in transmission coefficient over its area. Even in this case, it follows that the probable (mean) reduction in energy of the beam due to the $(m + 1)$th particle is exactly equal to $(E_m/E_0)\,\eta$, where η is the energy absorbed by a single disc when a uniform beam of unit intensity falls on it. In order to bring out the physical ideas clearly, some simple examples are worked out below directly without reference to the general theorem.

2. Simple One-Dimensional Analogue—the Strip Problem

Suppose there is a straight slit PQ of length L having uniform width and suppose we throw opaque strips each of length l whose width is larger than that of the aperture, such that they fall on the aperture with their length parallel to the length of the aperture, but with their centres distributed completely at random within the length L_0 (Fig. 1).

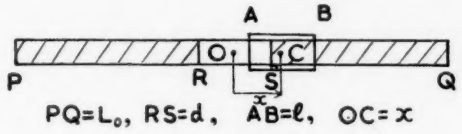


Fig. 1

Consider the situation after m strips are thrown. Some of them will overlap, and in general, there will be a number of gaps R_iS_i ($i = 1$ to k) of length d_i which are uncovered. Let $L_m = \sum_1^k d_i$ be the total uncovered length. Let the $(m+1)$th strip AB be now thrown and let the probability $p(x)\,dx$ of its falling with its centre C in an interval dx within PQ be given by $p(x)\,dx = k\,dx$, where k is a constant. (Note that we are now neglecting boundary effects.) In order to work out the mean additional length that is covered by this strip, consider one of the gaps R_iS_i which we will denote by RS for convenience, and let its length be d (Fig. 1). Suppose that it is the only gap in the slit, and denote the position of the new strip AB by the co-ordinate x of its centre C measured from the centre O of RS (Fig. 1). Then, denoting the additional length that is covered by this strip for different values of x by $f(x)$ the function $f(x)$ will vary as follows:

(*a*) $d > l$

$$f(x) = 0 \text{ for } x < -\left(\frac{d+l}{2}\right) \text{ and } x > +\left(\frac{d+l}{2}\right)$$

$$f(x) = l \text{ for } -\left(\frac{d-l}{2}\right) \leqslant x \leqslant \left(\frac{d-l}{2}\right)$$

and $f(x)$ varies linearly in the intermediate positions

(*b*) $d < l$

$$f(x) = 0 \text{ for } x < -\left(\frac{l+d}{2}\right) \text{ and } x > \left(\frac{l+d}{2}\right)$$

$$f(x) = d \text{ for } -\left(\frac{l-d}{2}\right) \leqslant x \leqslant \left(\frac{l-d}{2}\right)$$

and $f(x)$ varies linearly in between.

The variations are shown schematically in Figs. 2 (*a*) and (*b*) from which the integral of $f(x)$ from $-(d+l)/2$ to $+(d+l)2$ is seen to be ld in both cases. Thus, the mean length that is additionally obscured by AB is

$$\frac{\int_P^Q f(x)\, p(x)\, dx}{\int_P^Q p(x)\, dx} = \frac{k \int_{-(d+l)/2}^{+(d+l)/2} f(x)\, dx}{k\mathrm{L}} = \frac{ld}{\mathrm{L}} = \left(\frac{d}{\mathrm{L}}\right) l \tag{8}$$

i.e., it is a fraction d/L of l.

Clearly, if more than one gap $\mathrm{R_iS_i}$ is present, the contribution from each gap of length d_i is equal to $(d_i/\mathrm{L})\, l$, so that the mean additional length cut off by the $(m+1)$th strip is

$$\frac{\Sigma d_i}{\mathrm{L}} l = \frac{\mathrm{L}_m}{\mathrm{L}} l. \tag{9}$$

Thus,

$$\mathrm{L}_{m+1} = \left(1 - \frac{l}{\mathrm{L}}\right) \mathrm{L}_m \tag{10}$$

or each additional strip cuts out, on the average, a fraction l/L of the uncovered area (neglecting boundary effects).

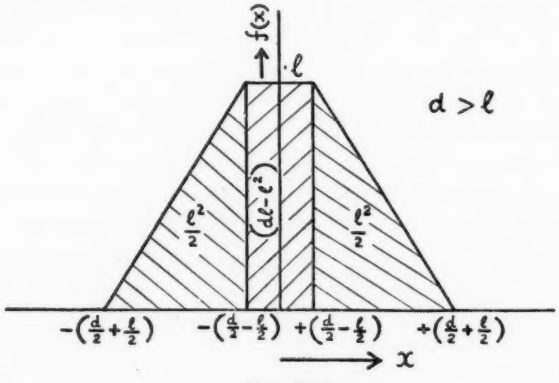


FIG. 2 (*a*)

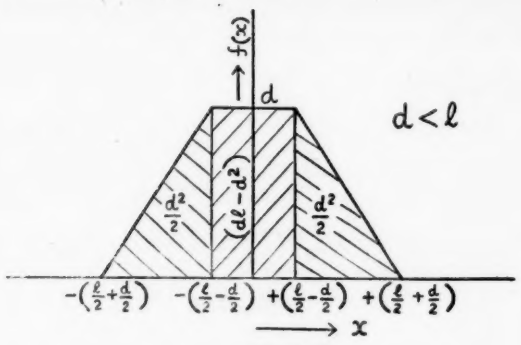


FIG. 2 (*b*)

The most interesting aspect of the above derivation is the fact that it does not depend on the magnitude of the length l of the strip and *the final result is true irrespective of whether it is larger or smaller than the individual gaps*. This comes because what is gained in the swings is lost in the roundabouts.

It might appear that such an exact balance will be possible only if there is a *linear* variation of $f(x)$ when it is varying, as is the case here. However, such a condition is not all necessary, as will be seen from the more general problem to be considered in the next section.

3. General One-Dimensional Case—Strip with Variable Absorption

Suppose in the example considered in Section 2, the strips are not opaque, but exhibit variations in transmission. This may be defined by a function $g(x')$ which gives the variation of the absorption coefficient, (*i.e.*, the fraction of the incident intensity that is absorbed) with distance x' from a chosen point (say the centre C of the strip). Thus, if light of intensity unity (per unit length of the slit PQ) is incident on the strip of length l, then the energy absorbed by it is

$$\eta = \int_{-l/2}^{+l/2} g(x')\,dx'. \tag{11}$$

Thus each strip absorbs an energy ηI where I is the incident (linear) intensity. We shall now consider what happens when the $(m+1)$th strip is added. Suppose light of (linear) intensity I is incident on the slit PQ. Then its total energy is $E_0 = LI$. Let the distribution of intensity along the length of the slit after m strips have been thrown be given by the function $h_m(x)$, x being

now measured from P [Fig. 3 in which the function $g(x')$ is also schematically represented]. Clearly,

$$E_m = \int_0^L h_m(x)\,dx. \tag{12}$$

Now, let the probability of the centre C of the $(m+1)$th disc falling in an interval dx at x be $p(x)\,dx = k dx$ as before. When it does fall there, the amount of energy removed from the transmitted beam is given by

$$\int_0^L g(x''-x)\,h_m(x'')\,dx'' = \int_{-\infty}^{+\infty} g(x''-x)\,h_m(x'')\,dx''$$
$$= gCh_m(x). \tag{13}$$

since $h_m(x'')$ is zero for values of x'' outside the range 0 to L.

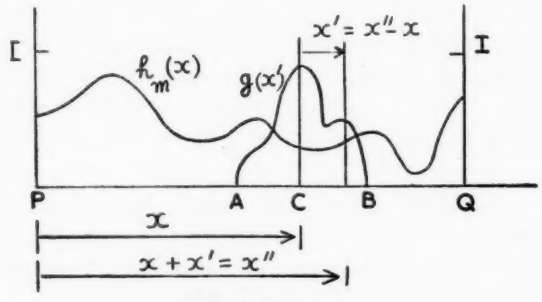


FIG. 3

The symbol gCh_m stands for the "correlation function" of the function $g(x)$ with $h_m(x)$ (see Appendix I for the definition of 'correlation function'). Since $g(x')$ becomes zero outside the length l of the strip, the limits of integration in the first expression in Equation (13) are justified if boundary effects are neglected.

The result (13) is for the case when the centre C of the strip falls at x. Consequently, the *mean* energy abstracted from the transmitted beam is obtained by averaging overall values of x from 0 to L. This gives a value

$$\frac{\int_0^L p(x)\,gCh_m(x)\,dx}{\int_0^L p(x)\,dx} = \frac{1}{L}\int_0^L gCh_m(x)\,dx. \tag{14}$$

By the correlation integral theorem discussed in Appendix I (Equation A 10) the last integral is equal to

$$\int_0^L h_m(x)\,dx \cdot \int_{-l/2}^{+l/2} g(x)\,dx = E_m\eta. \tag{15}$$

Thus, the mean reduction in energy due to the $(m + 1)$th strip is $\eta E_m/L$ or

$$E_{m+1} = \left(1 - \frac{\eta}{L}\right) E_m \tag{16}$$

which, by iteration, leads to the result

$$E_n = \left(\frac{1 - \eta}{L}\right)^n E_0. \tag{17}$$

It will be noticed again that Equation (16) is true irrespective of the nature of the variations of the functions $h_m(x)$ and $g(x)$. This is analogous to the result found for the opaque strip, namely, that the relative dimensions of l and the widths d_i of the various gaps is immaterial to the problem. Thus, the intensity may fluctuate to any extent over the length of the slit and the transmission of the strip AB may also widely vary over its length, but these are immaterial to the problem so long as we are interested only in the probable (or mean) reduction in energy due to the $(m + 1)$th strip. The mean reduction $(E_m - E_{m+1})$ is then simply a fraction η/L of the total energy content E_m.

The interesting point is that the evaluation of the function (13), giving the reduction in intensity when the centre of the strip falls at x, may be extremely difficult in any practical case. However, the theorem of Appendix I reduces the mean of this to an extremely simple form, namely, to the evaluation of the transmission of a single strip when kept in a uniform beam. Thus, we are able to show that Equation (16) is exactly true, analogous to Equation (10).

Incidentally, the centre C of the strip AB may be replaced by any fixed point on the strip in the above derivation and all the results would still be true. This is of interest in connection with the generalisation to two dimensions.

4. Extension to Two Dimensions—the Disc Problem

We shall now return to the disc problem, but will no longer restrict ourselves to circular discs. On the other hand, suppose that the discs are of arbitrary shape, but that they are all identical in shape and size (each of area a) and that they fall in exactly the same orientation on the area A, but at random positions. The randomness may be specified by stating that the probability that a chosen point on the disc falls in an area dA at $\mathbf{r}$ is equal to $K dA$, where K is a constant.

Let us denote the uncovered regions after m disc are thrown by A_m, and use A_m to denote also their area. Analogously to the strip problem,

we shall prove that the *mean* additional area that is covered by the $(m+1)$th disc is $(A_m/A)\,a$. A reference to Fig. 4 will show how surprising this result is at first sight, all the more so, since an attempt at proving this directly even for a circular disc turns out to be very difficult, because the shape of the individual apertures in the region A_m cannot be specified analytically.

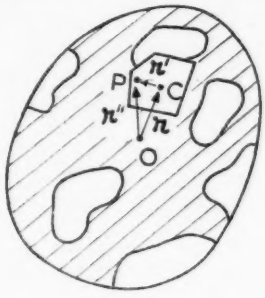


FIG. 4

We shall, therefore, prove a very general result by resorting to the theorem on the integral of convoluted functions and then deduce the above as a special case. Consequently, let the function $g(\boldsymbol{r}')$ denote the variation of absorption on the disc, the vector $\boldsymbol{r}'$ being measured from a specified origin C on the disc. Similarly let $h_m(\boldsymbol{r})$ be the distribution of intensity over the plane of the area A, after m discs are thrown, $\boldsymbol{r}$ being measured from an origin O on it. Clearly

$$E_m = \int_A h_m(\boldsymbol{r})\, d\boldsymbol{r}. \tag{18}$$

(Here $d\boldsymbol{r}$ denotes an element of area dA as in Appendix I.) Now, let the $(m+1)$th disc be thrown. Then for a particular position of this disc with $\overrightarrow{OC} = \boldsymbol{r}$, the energy absorbed by the disc is analogous to Equation (13),

$$\int_A h_m(\boldsymbol{r}'')\, g(\boldsymbol{r}'' - \boldsymbol{r})\, d\boldsymbol{r}'' = gCh_m(\boldsymbol{r}). \tag{19}$$

Consequently, the mean energy abstracted from the beam by the $(m+1)$th disc is similar to Equation (14) and is equal to

$$\frac{1}{A}\int_A gCh_m(\boldsymbol{r})\, d\boldsymbol{r}, \tag{20}$$

which by the correlation-integral theorem (A 20) of Appendix I, is equal to

$$\frac{1}{A}\cdot\int_A h_m(\boldsymbol{r})\, d\boldsymbol{r}\cdot\int_a g(\boldsymbol{r})\, d\boldsymbol{r} = \frac{E_m\eta}{A} \tag{21}$$

where

$$\eta = \int_a g(\boldsymbol{r})\, d\boldsymbol{r} \tag{22}$$

is the energy absorbed by one disc when unit intensity is incident on it.

Hence,

$$E_{m+1} = E_m \left(1 - \frac{\eta}{A}\right) \tag{23}$$

and by iteration

$$E_n = E_0 \left(\frac{1-\eta}{A}\right)^n. \tag{24}$$

Clearly, when the discs are opaque, η is just equal to a the area of the disc, and Equation (22) reduces to the form of Equation (3). The result is however true for a disc of any shape.

As stated in Appendix I, the correlation-integral theorem is true even if the two functions which are convoluted are functions of any number of variables. However, there is no analogue of the light transmission problem in three dimensions of real space.

5. Discussion

We had neglected the boundary effects in all the previous sections. The variations occurring near the boundary would have negligible effects only if the area a is small compared with the total area A (similarly for the one-dimensional case). However, the main point of the results proved above is that the variations *inside* the area A all get averaged out exactly, irrespective of the shape or nature of the discs and of the individual apertures within A, *provided we assume that the probability of a chosen point on the disc occurring anywhere within the area A is a constant*. If this last proviso is satisfied, all our results are mathematically correct. Thus, this condition is satisfied in the case of a light beam passing through a random cloud of particles of uniform density when the cross-section of the beam is completely inside the cloud.

It is interesting to note that although the phenomenon in its elementary form is subtractive, *i.e.*, each disc removes a certain amount of energy from the beam, the effect of each additional disc is found to be multiplicative owing to probability effects, when the average is taken. It would be of interest to study the *distribution* of the energy E_n after encountering n discs, quite apart

from its mean value, which we have shown is equal to $E_0 (1 - \alpha/A)^n$, but this is not attempted here.

The case when the particles of arbitrary but identical shape and size take up not only a random position within the area A, but also a random orientation, can also be readily worked out. Since for a definite orientation the mean follows the iterative formula (23), it undergoes no further change when averaged over all possible orientations. Consequently, Equation (24) still holds for E_n and the only relevant factor is η, the absorption factor for each disc.

The case when the particles vary in size has been treated in the earlier paper by the author when the size is small. A study of the proof shows that the results are equally valid when the size is not small, and by following arguments similar to those in the last section, it is possible to show that the following equations hold for the mean energy:

$$E_m = E_{m-1}\left(\frac{1 - \eta_m}{A}\right) \tag{25}$$

and

$$E_n = E_0\left(1 - \frac{\eta_1}{A}\right)\left(1 - \frac{\eta_2}{A}\right) \cdots \left(1 - \frac{\eta_n}{A}\right) \tag{26}$$

where η_i is the energy that would be absorbed by the ith disc if unit intensity is incident upon it.

ACKNOWLEDGEMENT

I wish to thank Dr. P. M. Mathews for the discussion I had with him which led to the development of these ideas.

REFERENCES

Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, 1943, **17 A**, 171.

Sneddon, I. N. .. *Fourier Transforms*, McGraw-Hill, New York, 1951.

APPENDIX

Faltung and Correlation Integral Theorems

1. Theorems on Faltung of Functions

The *Faltung* (convolution) of two functions $g(x)$ and $h(x)$ of a single variable x, denoted by $gFh(x)$ [$= f(x)$ say] is defined by*

$$gFh(x) = f(x) = \int_{-\infty}^{+\infty} g(x')\, h(x - x')\, dx', \tag{A 1}$$

which is also equivalent to the form

$$f(x) = \int_{-\infty}^{+\infty} g(x - x'')\, h(x'')\, dx''. \tag{A 2}$$

It is obvious that the functions gFh and hFg are identical.

Although the limits $-\infty$ and $+\infty$ is used for the integral, in practice both functions might be zero beyond finite limits, in which case the faltung $f(x)$ would also have a non-zero value only within finite limits. In such a case, it would be sufficient to evaluate the integral (A 1) or (A 2) within those limits.

It is possible to show that the *integral of the faltung of two functions is the product of the integrals of the individual functions.* We shall call this the Faltung Integral Theorem. If we restrict ourselves to functions which occur in physical problems, the only conditions required for its validity appear to be that the integrals of $g(x)$ and $h(x)$ should be finite.

Let

$$G = \int_{-\infty}^{+\infty} g(x)\, dx \quad \text{and} \quad H = \int_{-\infty}^{+\infty} h(x)\, dx.$$

Then,

$$F = \int_{-\infty}^{+\infty} f(x)\, dx = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} g(x')\, h(x - x')\, dx'$$

$$= \int_{-\infty}^{+\infty} g(x')\, dx' \int_{-\infty}^{+\infty} h(x - x')\, d(x - x') = GH. \tag{A 3}$$

* To avoid confusion with the use of the star for the complex conjugate and also so as to be in accordance with the notation of the correlation function below, the symbol gFh is used in preference to $g * h$ for the faltung of the functions g and h.

The condition for this to be valid is that the change in the order of integration in (A 7) should be justified which is ordinarily valid for physical functions.

Although the result (A 3) is a consequence of a well-known theorem on the Fourier transform of the convolution of two functions [*see e.g.*, Sneddon (1951)], it does not seem to have been specifically noted and applied so far. It appears to have applications in various physical problems.

If g and h are functions of a number of variables x_j (which may be collectively represented by a vector $\boldsymbol{r}$), then the following results hold. Define the faltung by

$$f(\boldsymbol{r}) = g\mathrm{F}h(\boldsymbol{r}) = \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} g(\boldsymbol{r}')\, h(\boldsymbol{r} - \boldsymbol{r}')\, d\boldsymbol{r}'. \tag{A 4}$$

Then, we have the general faltung integral theorem

$$\mathrm{F} = \mathrm{GH} \tag{A 5}$$

where

$$\mathrm{F} = \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} g(\boldsymbol{r})\, d\boldsymbol{r} \tag{A 6}$$

and similar integrals define G and H.

2. Theorems on Correlation Functions

It will be noticed that the integrals (13) and (19) in the body of the paper are very similar to that in the definition of the faltung function, but are different from the latter. In fact, integrals of the type met with in this paper also occur in other physical problems and it would be worthwhile to define a function, which may be called the 'correlation function'.

The "correlation function of $g(x)$ with $h(x)$" denoted by $g\mathrm{C}h(x)$ is defined by

$$g\mathrm{C}h(x) = \int_{-\infty}^{+\infty} g(x')\, h(x + x')\, dx' \tag{A 7}$$

Clearly Equation (A 7) is also equivalent to the form

$$g\mathrm{C}h(x) = \int_{-\infty}^{+\infty} g(x'' - x)\, h(x'')\, dx'' \tag{A 8}$$

However, $gCh(x)$ is not necessarily equal to $hCg(x)$, but

$$gCh(x) = hCg(-x) \tag{A 9}$$

The term " correlation " for the function $gCh(x)$ is justified by the fact that the value of this function at x is obtained by taking the product of g at x' and of h at $x + x'$, *i.e.*, obtained by an additional shift x, and integrating over x'.

The correlation function of $g(x)$ with $h(x)$ can be shown to be equal to the faltung of $g(-x)$ and $h(x)$. Hence, from the faltung integral theorem

$$\int_{-\infty}^{+\infty} gCh(x)\,dx = \int_{-\infty}^{+\infty} g(-x)\,dx \cdot \int_{-\infty}^{+\infty} h(x)\,dx = \mathrm{GH}. \tag{A 10}$$

Thus, the integral of the correlation function of g with h is also equal to the product of the two integrals of the functions g and h separately. We shall call this the *Correlation Integral Theorem*. It will be noticed that the integrals which occur in the body of the paper are all of the type defining a 'correlation function'. Since these functions vanish outside a finite range of the argument, the limits in (A 10) can be set finite in these cases. The extension of theorem to a number of independent variables x_i is obvious.

Only the results required for the present paper have been derived in this Appendix. It is proposed to discuss the properties of the faltung function and the correlation function in a separate paper with examples of their applications in physical problems.

745–60 Printed at the Bangalore Press, Bangalore City, by T. K. Balakrishnan, Superintendent,
and Published by The Indian Academy of Sciences, Bangalore

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably) twice the size than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of author; Name of Journal (abbreviation) with a single underline; Year of publication; Number of Volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Fifty free reprints including plates and with cover will be supplied for each paper. Additional copies can be supplied at cost on previous intimation.

Blocks appearing in the *Proceedings* will be available for purchase by their respective authors. Orders for the same should be sent along with the corrected proofs and in any case not later than one month after the date of publication of the paper. The price charged would be 25% of the actual cost of the blocks *plus* freight and despatching charges. If the blocks are reproduced in other journals or publications, due acknowledgment should be made in them to the *Proceedings*.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

PAGE

On the System and Engineering Design of the General Purpose Electronic Digital Computer at T.I.F.R. . . . . R. Narasimhan 47

Studies on Metallic Halide Dioxanates—III. Dioxanates of Cobalt (ii) and Nickel (ii) Chlorides . Miss Sosamma Chandy and S. S. Moosath 58

dl-Marindinin (Dihydrokawain) and Some Related 6-Aryl-5, 6-Dihydro-4-Methoxy-2-Pyrones . . . K. Viswanathan and S. Swaminathan 63

A Critical Appraisal of Some Cosmic Ray Data for the I.G.Y. . R. P. Kane 69

Studies on Collagen. VI. Influence of Lyotropic Salt Solutions on the Optical Activity of Collagen . . . . . S. Venkataraman 83

A Problem in Probability Related to the Passage of Light through a Cloud of Particles . . . . . G. N. Ramachandran 87